Volume 52 September-October 1957 Number 6

Economic Geology

and the

Bulletin of the Society of Economic Geologists

CONTENTS

Alteration of Sandstone As a Guide to Uranium Deposits and Their Origin, Northern Black Hills, South Dakota ... *R. C. Vickers* 599
The Paragenetic Relationships of Germanite and Reniérite from Tsumeb, South West Africa ... *Charles B. Sclar and Bruno H. Geier* 612
Anhydrite Complex of the Morococha District, Peru ... *R. H. Nagell* 632
The Occurrence of Zinc in Soil ... *M. L. White* 645
Heavy Metal Concentration in Streams in North Angola ... *D. J. Atkinson* 652
On the Occurrence of Uranium in Ancient Conglomerates ... *Charles F. Davidson* 668
Reflecting Curved-Crystal X-Ray Spectograph—A Device for the Analysis of Small Mineral Samples ... *I. Adler and J. M. Axelrod* 694
The Odara Pegmatite ... *C. V. Paulose* 702
Scientific Communications:
A Suggested Interpretation of the Quebec-Labrador Iron Deposits ... *G. Vibert Douglas and L. P. Compton* 709
Discussions:
Geotectonics and Uranium Mineralization, Australia ... *B. P. Walpole* 712
Pitchblende-Bearing Veins, Central City District, Colorado ... *John S. Vanderpool* 713
Sulfur Isotopes: A Reply to Professor McKinstry ... *Herbert W. Feely, J. Laurence Kulp and Wayne U. Ault* 713
Heat and Temperature in Ore Deposition ... *Hironao Nishihara* 715
Is Leucoxene Always Finely Crystalline Rutile?—A Reply ... *Sturges W. Bailey and Eugene N. Cameron* 716
Reviews:
Geology of Uranium and Thorium (Compiled by L. R. Page, H. E. Stocking and H. B. Smith) ... *William T. Holser* 721
Geologicheskaya Literatura SSSR. 1956, No. 1 ... 723
Geology and Mineral Resources of the Ivanpah Quadrangle, California and Nevada (D. F. Hewett) ... *Lauren A. Wright* 723
Principles of Stratigraphy (Carl O. Dunbar and John Rodgers) ... 724
Prospektion von Uran- und Thoriumerzen (G. Zeschke) ... 725
Geologic Field Methods (Julian W. Low) ... 725
Geology of India and Burma (M. S. Krishnan) ... 725
The Living Rocks (Stévan Célébonovic) ... 726
The Exploration of the Colorado River (John Wesley Powell) ... 726
Introduction à L'Étude des Roches Métamorphiques et des Gites Métallifères. (Pierre Laffitte) ... 727
Books Received ... *James M. Allen and John W. Salisbury* 727
Society of Economic Geologists:
Program of Annual Meeting, Atlantic City, Nov. 4–6, 1957 ... 733
Scientific Notes and News ... 736

PUBLISHED SEMI-QUARTERLY

Six Dollars Fifty Cents a Year, One Dollar Twenty-five Cents a Copy

THE ECONOMIC GEOLOGY PUBLISHING COMPANY

Printed by Lancaster Press, Inc., Prince and Lemon Streets, Lancaster, Pa.

Entered as second-class matter, March 30, 1906, at the Post Office at Lancaster, Pa., under the Act of Congress of March 3, 1879

Economic Geology

and the

Bulletin of the Society of Economic Geologists

Issued Semi-Quarterly and sent to subscribers on or about the following dates: February 1, March 15, May 1, June 15, August 1, September 15, November 1, December 15.

Manuscripts for publication should be sent to the Editor, **ALAN M. BATEMAN, at Yale University, Yale Station, New Haven, Conn.** It is requested that contributors exercise care in writing *scientific* and *proper names*. References to other publications should be in accordance with the forms used in the pages of this journal. The manuscript should be typewritten with double space lines and must be preceded by *a brief abstract*. Galley proof will be sent authors only where a request to this effect accompanies the manuscript, or when, in the editor's opinion, the subject matter is such as will require correction by the author.

Reviews should conform to the journal usage. Review Committee: The Editor, C. H. Behre, L. C. Graton, J. T. Singewald, Jr., J. Gilluly, A. F. Buddington, W. H. Newhouse.

Books and Pamphlets for review should be sent to the Editor.

Reprints. Contributors desiring reprints of their papers may obtain them by filling out the order slip which will be attached to the galley proof when it is sent to the author. Provided the order slip is received by the editor, *with the return of the proof*, 50 reprints without covers will be furnished without charge. Reprints of discussions and informal communications are not furnished free of charge except when they exceed four pages in length when 50 will be supplied without charge. Reprints of reviews are not supplied. Additional reprints will be furnished at approximately the rates given in the table below (effective with No. 5) when ordered *in advance of publication*. The rates apply only to plain text, with line engravings. Papers containing folded maps or plates will be more expensive.

The following rates do not include free carriage. *Postage or express must be paid by the author.*

	4 pp. 1–4	8 pp. 5–8	12 pp. 9–12	16 pp. 13–16	20 pp. 17–20	24 pp. 21–24	28 pp. 25–28	32 pp. 29–32	Covers
50 copies.....	$4.20	$6.65	$10.40	$10.85	$14.15	$16.25	$18.70	$19.95	$5.75
100 "	5.00	7.95	12.00	13.30	17.00	19.95	23.30	25.00	7.80
Additional copies per C.	1.70	2.55	4.20	5.00	5.85	7.50	9.15	10.00	3.75

For 500 copies deduct 5%; for 1000 copies or more deduct 10%. For more than 32 pages add cost per schedule to make total. Example: For 44 pages add cost for 32 pages and 12 pages. The 50 copy price is the minimum charge.

Covers: Standard covers are of the same style of type and paper as the cover of the journal, and bear the title of the article and name of its author. Special printing on cover is charged for at the cost of composition.

Plates are $4.20 for the first 50 if printed on one side, and $3.15 per "C" for additional's; printed on both sides, $6.30 for the first 50, and $4.70 per "C" for additional's.

Collotype plates are 8 cents each for each additional reprint over the 50 copies furnished free. Example: An extra 50 reprints containing one collotype plate would cost $4.00; 2 collotype plates, $8.00.

Note: For any reprints requiring additional composition or changes, either in text or cover, an extra charge will be made.

The retail prices of single reprints when available from the office of the Business Manager are as follows:

1–4 pp. 15c	5–8 pp. 20c	9–12 pp. 25c	13–20 pp. 30c	21–28 pp. 35c
29–36 pp. 40c	37–44 pp. 45c	45–52 pp. 50c	53–60 pp. 55c	61–68 pp. 60c

Subscriptions. The price of the journal to subscribers in the United States and its dependencies is $1.25 for a single copy, or $6.50 a year for eight numbers effective July 1, 1953. To subscribers in Canada, Cuba, Mexico, Spain, and countries in Central and South America, except Dutch and French Guiana, the annual rate is $6.80; to other countries, $7.25.

Forwarding. Subscribers wishing their journal to be forwarded to a new address should leave postage for that purpose with the Postmaster at their old address.

Missing numbers will be replaced without charge if claim is made within four weeks after the date of issue of the following number, provided that the neglect to receive them is not due to neglect to arrange for their forwarding.

Remittances should be made payable to the **ECONOMIC GEOLOGY PUBLISHING COMPANY**, and should be mailed to **M. M. LEIGHTON**, Business Manager, Urbana, Illinois, to whom also all **Business Communications** should be addressed.

Foreign Agents. The Technical Bookshop, Salisbury House, London Wall, London E. C. 2, England, British Agents.

Indexed in the Industrial Art Series.

LANCASTER PRESS, INC., LANCASTER, PA.

ECONOMIC GEOLOGY

AND THE

BULLETIN OF THE SOCIETY OF ECONOMIC GEOLOGISTS

EDITOR: ALAN MARA BATEMAN
Yale University, New Haven, Connecticut

BUSINESS EDITOR: MORRIS M. LEIGHTON
Illinois Geological Survey, Urbana, Illinois

ASSISTANT EDITORS

H. E. MCKINSTRY, *Harvard University*
JOE W. PEOPLES, *Wesleyan University*
M. LEROY JENSEN, *Yale University*
J. D. BATEMAN, *Toronto, Ont.*
R. H. JAHNS, *California Institute of Technology, Pasadena*

ASSOCIATE EDITORS

D. F. HEWETT
U. S. Geological Survey, Menlo Park, Calif.

A. I. LEVORSEN
Tulsa, Okla.

B. S. BUTLER
Univ. of Arizona, Tucson, Ariz.

W. E. WRATHER
Washington, D. C.

A. N. SAYRE
U. S. Geological Survey, Washington, D. C.

L. C. GRATON
Orange, Connecticut

E. S. MOORE
Univ. of Toronto, Toronto, Can.

GEORGE W. MOREY
Geophysical Laboratory, Washington, D. C.

PER GEIJER
Djursholm, Sweden

P. F. FOURMARIER
Liège University, Liège, Belgium

M. S. KRISHNAN
Ministry Natural Resources and Scientific Research, New Delhi, India

T. W GEVERS
University of the Witwatersrand, Johannesburg, S. Africa

C. F. DAVIDSON
St. Andrews Univ., Fife, Scotland

J. A. BROGGI
Instituto Geologica, Lima, Peru

TAKEO WATANABE
University of Tokyo, Tokyo, Japan

KONRAD B. KRAUSKOPF
Stanford University, California

A SEMI-QUARTERLY JOURNAL PUBLISHED BY
THE ECONOMIC GEOLOGY PUBLISHING COMPANY

SOCIETY OF ECONOMIC GEOLOGISTS

THE PUBLICATIONS OF WHICH CONSTITUTE
A PART OF THIS JOURNAL

OFFICERS FOR 1957

GILBERT H. CADY, *President*

W. D. JOHNSTON, JR., *Vice President*

HAROLD M. BANNERMAN, *Secretary*, U. S. Geological Survey, Washington 25, D. C.

JOSEPH T. SINGEWALD, JR., *Treasurer*, Johns Hopkins University, Baltimore 18, Maryland

Councilors

1957	*1958*	*1959*
R. F. BAKER	F. S. TURNEAURE	JAMES BOYD
JOHN W. VANDERWILT	DONALD M. FRASER	DUNCAN R. DERRY
THOMAS L. KESLER	CHARLES MEYER	W. H. CALLAHAN

Regional Vice Presidents

CHARLES F. DAVIDSON, Europe.....JORGE A. BROGGI, South America
R. A. PELLETIER, Africa.....JENARO GONZALEZ-REYNA, North America
HAROLD G. RAGGATT, Australia.....TAKAO SAKAMOTO, Asia

Executive Committee

GILBERT H. CADY, *Chairman* — FRANCIS CAMERON — GEORGE M. SCHWARTZ
JOSEPH T. SINGEWALD, JR. — W. D. JOHNSTON, JR. — HAROLD M. BANNERMAN

President's appointments to Committees for 1957–58

Finance Committee

DONALD M. FRASER, *Chairman* — ROBERT P. KOENIG
JOSEPH T. SINGEWALD, JR.

Program Committee

JOHN H. MELVIN, *Chairman* — MEREDITH E. JOHNSON
ROBERT M. GROGAN — KENNETH C. COCHRAN
BYRAN N. COOPER — HAROLD M. BANNERMAN, *Ex-officio*
THOMAS E. GILLINGHAM

Committee on Publications

L. W. CURRIER, *Chairman* — ROBERT M. GARRELS — D. J. FISHER

Nominating Committee

JOSEPH T. SINGEWALD, JR. — M. M. LEIGHTON — T. B. NOLAN

Admissions Committee

F. S. TURNEAURE, *Chairman* — ROBERT M. DREYER — CHARLES S. BLAIR
CLAYTON C. BALL — JOSEPH L. GILLSON

Auditing Committee

FRANCIS G. WELLS, *Chairman* — A. NELSON SAYRE

Coal Research Committee

ROBERT M. KOSANKE, *Chairman* — IRVING M. BREGER
CHARLES E. WIER — JAMES M. SCHOPF

ORDER BLANK

FIFTIETH ANNIVERSARY VOLUME
ECONOMIC GEOLOGY
1905-1955

(See page ii)

☐ Enclosed is $..... ☐ Enter my order and send bill

☐ Price to Subscribers $6.00

(including Members, Non-Member Journal Subscribers, and Students whether subscribers or not)

☐ Price to Non-Subscribers to Journal $8.00

To Economic Geology Publishing Company
105 Natural Resources Building
Urbana, Illinois

Mail above copy as checked to:

Name

Street Address

City State Country

ECONOMIC GEOLOGY

AND THE

BULLETIN OF THE SOCIETY OF
ECONOMIC GEOLOGISTS

VOL. 52 SEPTEMBER–OCTOBER NO. 6

ALTERATION OF SANDSTONE AS A GUIDE TO URANIUM DEPOSITS AND THEIR ORIGIN, NORTHERN BLACK HILLS, SOUTH DAKOTA[1]

R. C. VICKERS

CONTENTS

	PAGE
Abstract	599
Introduction	600
Location and general features	600
Geology	600
Fall River sandstone	601
Uranium deposits	602
Alteration of sandstone	603
Nature of the red-buff contact	604
Mineralogy of the red and buff sandstones	605
Relationship of uranium mineralization to the red-buff contact	605
Relationship of the red-buff contact to structure	605
Relationship of thickness to red-buff contact and uranium deposits	606
Relationship of uranium deposits to structure	606
Origin of the uranium deposits	607
Origin of the red alteration	610
Source of the uranium	611
Acknowledgments	611
Literature cited	611

ABSTRACT

Several uranium deposits are present in the Fall River sandstone of Early Cretaceous age on the northeast flank of the Black Hills, Butte County, South Dakota. The deposits are within a fine-grained, well-sorted, persistent basal sandstone unit that ranges in thickness from 2 to 18 feet and dips about 4° NE.

Detailed mapping of about 2 square miles surrounding the deposits has shown that all the uranium occurrences and most of the areas of high radioactivity are where the color changes in the basal sandstone from red-

[1] Publication authorized by the Director, U. S. Geological Survey.

dish on the up-dip side of the occurrences to yellowish-gray or buff down-dip. Radioactivity measurements show that uranium is distributed almost continuously along the sinuous red-buff contact for more than 5 miles. Laboratory work indicates that the red color is caused by hematite resulting from the alteration of ferrous iron minerals and hydrous ferric oxides.

The close association of the red-buff contact and the uranium deposits suggests that the two were formed by the same solutions. The uranium was probably deposited originally from ground water that moved down-dip and gradually changed from an oxidizing solution near the surface to a mildly reducing solution at depth. Concentrations of uranium have resulted from the localization of reducing conditions caused perhaps by structures superimposed on the regional dip, local thinning or decrease in permeability of the sandstone, or concentrations of pyritiferous carbonaceous material.

The red alteration is probably the result of pre-Oligocene weathering that has extended downward in the more permeable beds about 200 feet below the ancient erosion surface.

Oxidation of the primary uranium during the present weathering cycle has resulted in the formation of carnotite and possibly other secondary uranium minerals.

INTRODUCTION

ABNORMAL radioactivity in southwestern Butte County, South Dakota, was first detected in August 1953 by light-plane airborne reconnaissance conducted by the U. S. Atomic Energy Commission. Later, ground reconnaissance by geologists of the Commission and prospectors resulted in the discovery of several small sandstone-type uranium deposits. During the winter of 1953–54, about 450 tons of rock containing between 0.1 and 0.2 percent uranium was mined from one of the deposits (Kling No. 2), and about 8 tons of similar-grade material was mined from the Bonato deposit. There has been no additional production from the area to date.

During August 1954, about 2 square miles surrounding the Kling and Bonato uranium deposits were mapped by the U. S. Geological Survey with plane table and alidade at a scale of 1 : 2,400 to determine ore controls that might be used as guides to find additional deposits.

Location and General Features.—The area of investigation is shown in Figure 1. The locality is on the northeast flank of the Black Hills uplift, about 6 miles west of Belle Fourche, and includes parts of secs. 23, 24, 25, and 26, T. 8 N., R. 1 E., Butte County, South Dakota.

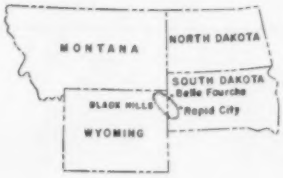
The area has a slightly undulating surface that slopes gently to the northeast and is dissected by numerous small canyons generally less than 150 feet deep. The average surface elevation is about 3,400 feet, and the total relief in the mapped area is about 900 feet.

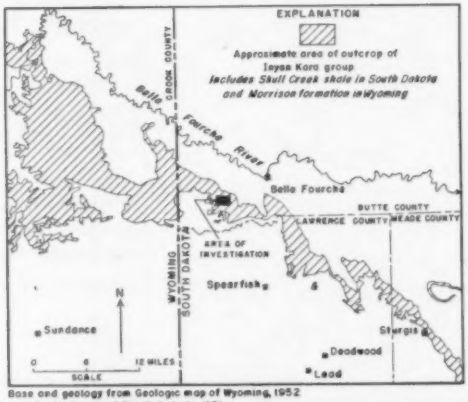
GEOLOGY

The general geology is relatively simple. The basal sandstone unit of the Lower Cretaceous Fall River sandstone of the Inyan Kara group forms an almost continuous outcrop along the canyon sides and rims. The Fuson shale, which underlies the Fall River sandstone, crops out in the lower parts of the canyons. The general stratigraphy of the area and a typical section in one

of the numerous small canyons are shown in Figure 2. The rocks dip about 4° NE and dip-slope surfaces are developed on sandstone beds of the Fall River sandstone in the intercanyon areas.

Fall River Sandstone.—The most persistent unit in the Fall River sandstone is the basal sandstone, which ranges from 2 to 18 feet in thickness but generally is from 6 to 10 feet thick, and is composed of fine-grained, massive, generally uniformly bedded buff to red sandstone. Size analyses show that the sand is well sorted; more than 95 percent of the grains are fine sand (¼





Base and geology from Geologic map of Wyoming, 1952 and Geologic map of South Dakota, 1951

FIG. 1.-INDEX MAP SHOWING LOCATION OF THE AREA OF INVESTIGATION, BUTTE COUNTY, S. DAK.

FIG. 1.

to ⅛ mm) and very fine sand (⅛ to 1/16 mm); the remainder is silt and clay. Carbonaceous plant fragments are locally abundant in small lenses or along bedding planes. Vertical holes, a few millimeters in diameter, some of which are partly filled with carbonaceous material, were observed in the upper few inches of the basal unit, and these may represent a carbonized root system. A thin bed of shaly lignite, a few inches to 1 foot thick, overlies the sandstone.

The lithology of the Fall River sandstone above the shaly lignite consists mainly of variable amounts of impure sandstones, siltstones, and shales. About 1 mile southeast of the Bonato ranch (Fig. 3), the upper part of the Fall River sandstone is well exposed and consists of 32 feet of gray to buff

siltstone and shale that contains a few thin beds of limestone from one-half inch to 5 inches thick near the top. The contact with the overlying dark-gray fissile Skull Creek shale was not observed. The thickness of the Fall River sandstone ranges from about 35 to 55 feet, depending largely on the thickness of a bluff to reddish-brown cross-bedded sandstone as much as 30 feet thick that in places is present in the upper part of the formation.

Uranium Deposits.—All the uranium occurrences in the mapped area are in the basal sandstone unit of the Fall River sandstone except at the Bonato mine, where small quantities of carnotite were found in sandstone immediately

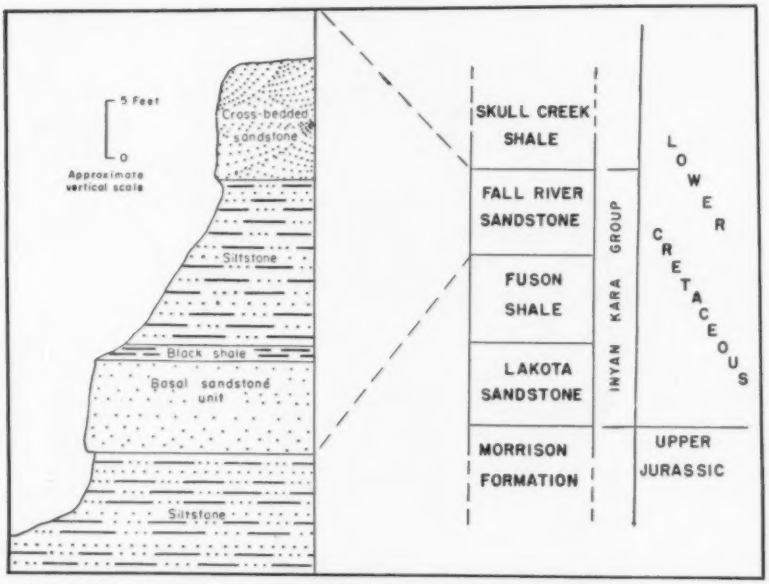


FIGURE 2.-GENERAL STRATIGRAPHIC SECTION, AND A TYPICAL COLUMNAR SECTION IN AREA OF INVESTIGATION, BUTTE COUNTY, SOUTH DAKOTA

FIG. 2.

above the shaly lignite which overlies the basal strata. However, the carnotite above the basal sandstone unit was localized along joints (oral communication from Clyde Boyle, mine operator) and may have been derived from the underlying sandstone by solution and redeposition.

Carbonized wood fragments are conspicuous at most of the carnotite occurrences. Carnotite is present as small pulverulent masses, as much as one-fourth inch in diameter, in carbonized wood fragments and as disseminations interstitial to, or coating, sand grains. The disseminated carnotite is commonly present in thin seams parallel to the bedding. The identification of the carnotite was confirmed by X-ray powder photographs.

With the exception of the Kling No. 2 mine (Fig. 3), where about 450 tons of ore was removed, all the uranium occurrences are small, and only a few tons of ore-grade material were evident from most of the surface exposures.

ALTERATION OF SANDSTONE

Pink sandstone associated with uranium deposits was first recognized by Bales (1, p. 221) in the southern Black Hills. In general, the pink sandstone is there restricted to the immediate vicinity of the uranium deposits; but, in

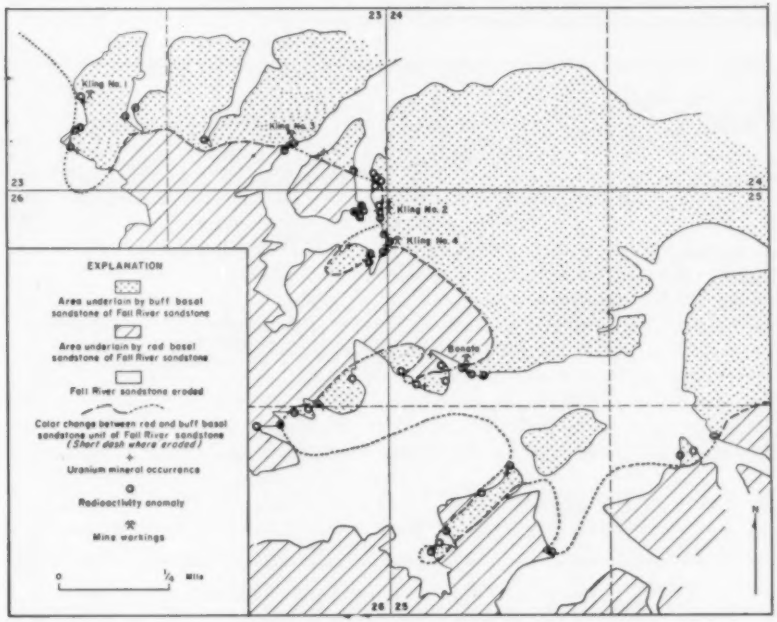


FIG. 3. Geologic map of the basal sandstone unit of the Fall River sandstone showing relationship of color change to radioactivity anomalies and uranium mineral occurrences, T. 8 N., R. 1 E., Butte County, South Dakota.

the northern Black Hills, in the area of this investigation reddish Fall River sandstone underlies several square miles or perhaps tens of square miles. Although it was realized from the previous work of Bell and Bales that the red sandstone might have some relationship to the uranium occurrences, the nature of this relationship was not appreciated until detailed mapping of the area had started. It then became apparent that most of the known uranium occurrences and radioactivity anomalies were in buff to gray sandstone immediately down dip from reddish altered sandstone. Both the buff and red sandstone are within the basal sandstone unit of the Fall River sandstone.

Nature of the Red-Buff Contact.—In most of the mapped area (Fig. 3) the color of the basal sandstone unit of the Fall River changes from gray (yellowish gray, 5Y 7/2; to grayish yellow, 5Y 8/4) [2] to reddish (grayish orange pink, 5YR 7/2; pale red 10R 6/2; to pale reddish brown, 10R 5/4) within a horizontal distance of several feet or a few tens of feet. Commonly the contact between dominantly red and dominantly buff sandstone can be located within about 30 feet. Size analyses of both the red and buff sandstones at the Kling No. 2 mine showed no significant differences. A cross-section of a typical red-buff contact in the basal sandstone unit of the Fall River sandstone is shown in Figure 4. The more intense red color of the altered sandstone is near the red-buff contact.

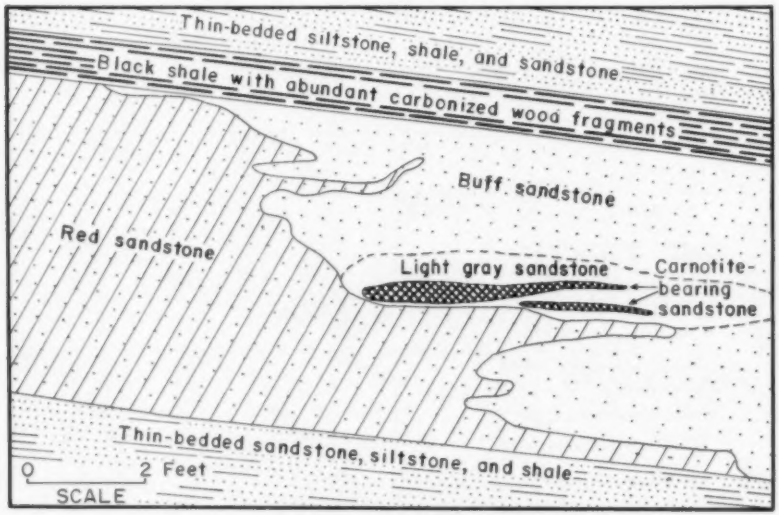


FIG. 4. Cross-section showing relationship of red-buff contact to carnotite-bearing sandstone.

Reddish color (pale red) was observed in the basal unit of the Fall River sandstone continuously for more than 1 mile to the southwest up dip from the red-buff contact. Reddish sandstone of the same sandstone unit was also observed a few miles both to the northwest and to the southeast of the mapped area.

In detail the reddish coloration of the sandstone at the red-buff contact cuts across the bedding and commonly extends farther down dip near the base of the sandstone. The red sandstone is believed to represent altered buff sandstone for the following reasons:

[2] Rock Color Chart designations, National Research Council.

a. The basal unit of the Fall River sandstone is predominantly buff to gray where it is exposed on the northeast flank of the Black Hills (from Rapid City to Belle Fourche).
b. The red-buff contact cuts across the bedding and the red sandstone is a uniform color as contrasted with the color differences of adjacent beds in the buff sandstone.
c. At several localities in the mapped area, color bands of various shades of red are parallel to the red-buff contact, and the more intense red color is near the red-buff contact.

Mineralogy of the Red and Buff Sandstones.—Laboratory study of the Fall River sandstone suggests that the red color is probably the result of the alteration of ferrous iron minerals and yellowish brown hydrous iron oxides to red hematite.

The relative total iron content in each of several samples of red, buff, and gray sandstone was determined by X-ray fluorescence, and the red color is not a function of the total iron present. The total iron present in the samples ranges from 0.1 to 0.5 percent. (Spectrographic analyses by K. E. Valentine and N. M. Conklin, U. S. Geological Survey.)

Samples of buff and gray sandstone were heated with a Meeker burner to about 600° C for 20 minutes. The red colors produced by the heating were almost identical to the red colors in the natural red sandstones. This suggests that the red color in the basal unit of the Fall River sandstone resulted from the alteration of hydrous ferric oxides, and ferrous iron compounds, to hematite. Heavy-mineral determinations show abundant magnetite in the heavy minerals from the buff sandstone, whereas practically no magnetite was found in samples of red sandstone. With the exception of the iron oxides, no differences in mineralogy were noted between samples of nonuraniferous buff and red sandstone.

Relationship of Uranium Mineralization to the Red-Buff Contact.—All the uranium occurrences that have been found in the area of this investigation are immediately adjacent to the red-buff contact and with one exception are in buff sandstone. Three previously unknown occurrences of carnotite were found on the basis of the red-buff color change. Abnormal radioactivity (greater than 10 times background) was detected with a scintillation counter at practically all outcrops of the basal sandstone unit of the Fall River sandstone that showed the red-buff contact. About 32 radioactive localities were found at these outcrops, which are distributed along the sinuous contact between red and buff sandstone for about 5 miles. Abnormal radioactivity was also detected at a red-buff contact in Fall River sandstone about 1 mile northwest of the mapped area on the north side of Hay Creek valley. Southeast of the mapped area for at least 2 miles the red-buff contact was not observed; all outcrops noted of the basal unit of the Fall River sandstone were red.

Relationship of the Red-Buff Contact to Structure.—As shown in Figure 5, the red-buff contact in general parallels the strike of the regional dip but in detail cuts across the smaller structures. Mapping in the area indicates that small structures have exerted little control of the red coloration in the

sandstone. An exception to this is in the SW¼ sec. 25, where unaltered buff sandstone occupies a structural trough that trends northeast.

Relationship of Thickness to Red-Buff Contact and Uranium Deposits.—The thickness of the basal sandstone unit of the Fall River sandstone was measured at most outcrops where the full thickness was exposed. In the northwestern half of the mapped area, which includes all of the Kling deposits, no relationship of thickness to the uranium occurrences is apparent. The basal sandstone in this area is from 8 to 13 feet thick. In the southeastern

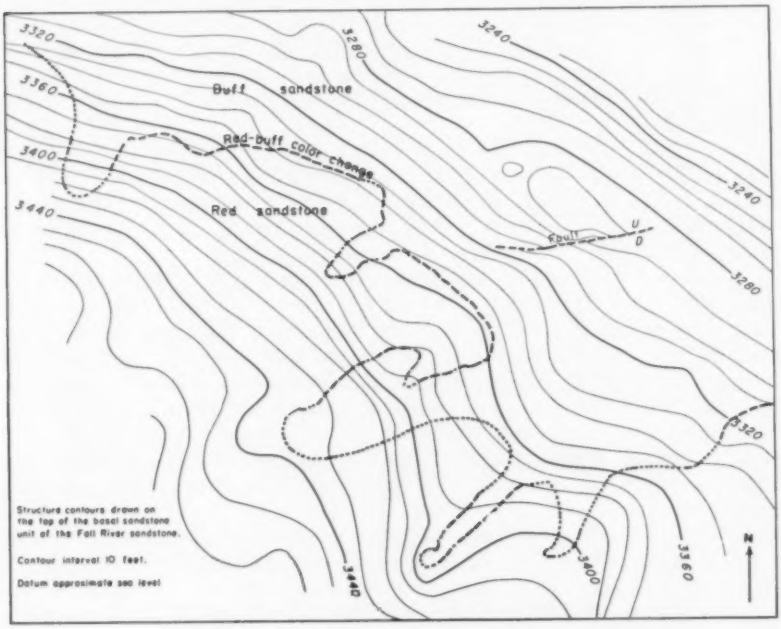


FIG. 5. Relationship of structure to red-buff color change. (Area shown is the same as that in Fig. 3.)

half of the mapped area, many of the radioactivity anomalies and all the carnotite occurrences (except at the Bonato mine) are in sandstone generally less than 5 feet thick. Exposures are commonly poor where the basal sandstone unit is thin, therefore its thickness could only be approximated in many places.

In general, where the basal sandstone unit is thick (more than about 5 feet) the red-buff contact is found farther down dip than in areas where the sandstone is thin (less than about 5 feet). This relationship would be expected if ground waters moving down dip have caused the alteration.

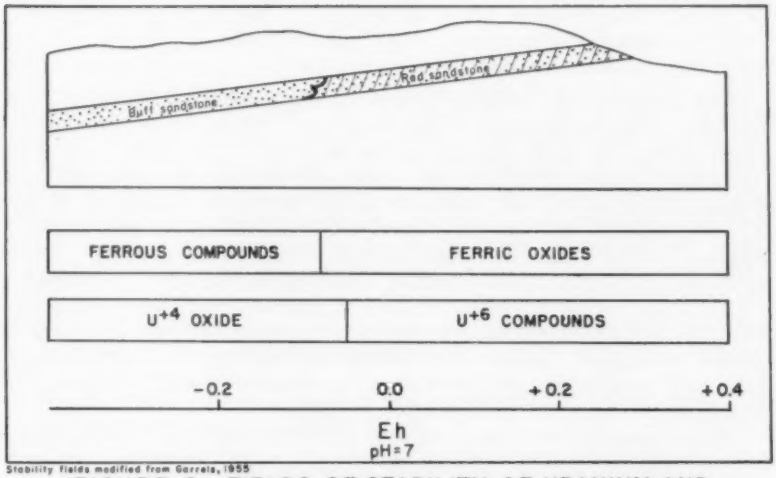
Relationship of Uranium Deposits to Structure.—Minor structural features may have localized some of the uranium deposits. At the Kling No. 4 mine

there is a local flattening of the regional dip; and for about 100 feet, measured perpendicular to the regional dip, there is a slight reversal of dip. The Kling No. 2 mine, about 200 feet down dip from the Kling No. 4 mine, and the Kling No. 3 mine are also on small structural terraces. Several of the other uranium occurrences appear to be where the dip is less steep or are immediately down dip from such areas.

The relationship between uranium deposits and structure is not marked, and the structural relationship noted above may be fortuitous. However, it may be significant that the largest uranium deposit (Kling No. 2) and the most widespread high radioactivity are down dip from the only observed reversal of dip found near the red-buff contact. Other uranium deposits of comparable size may not be present because other favorable structures are lacking.

ORIGIN OF THE URANIUM DEPOSITS

The red alteration described in this paper may have significance relative to the origin of the uranium deposits. If one assumes that the uranium was deposited from the same solutions that produced the red alteration—and the close association of the uranium with the red-buff contact strongly suggests



Stability fields modified from Garrels, 1955

FIGURE 6.-FIELDS OF STABILITY OF URANIUM AND IRON AS APPLIED TO THE RED-BUFF CONTACT

this—then the uranium-bearing solutions moved generally down-dip. This direction would also be expected of normal ground-water flow in the area.

Because most of the uranium was deposited not in the red sandstone but immediately down-dip from the red-buff contact, alteration and uranium deposition probably occurred under different chemical conditions. Both field and laboratory evidence suggest that the uranium was transported in the

hexavalent state and deposited as pitchblende from downward-moving solutions that underwent reduction. Oxidation of the pitchblende during the present weathering cycle has resulted in the formation of carnotite and possibly other secondary uranium minerals.

The stability fields of uranium and iron minerals are consistent with this theory. Figure 6 shows the fields of stability of uranium and iron minerals as applied to the red-buff contact at a pH of 7. Similar relations would exist at other pH values. These relations suggest that pitchblende or perhaps coffinite was the original stable uranium mineral deposited because U^{+4} oxide (pitchblende) would be the stable uranium mineral in the buff sandstone that contains dominantly ferrous iron minerals below the zone of oxidation.

Because the stability fields of ferric oxide and U^{+4} oxide overlap only within a narrow range of Eh values that are more reducing than conditions usually found under near-surface oxidizing conditions, it is reasonable to assume that the uranium was transported in the hexavalent state.

A laboratory experiment was conducted to determine the oxidation potential (Eh) and pH of waters in equilibrium with samples of both the buff and red sandstones. The samples of sandstone were sealed in glass containers with sufficient water to cover the samples. The Eh and pH of the solutions were measured after a period of six months with the following results:

	pH	Eh (volts)
Buff sandstone	6.80	+.084
Red sandstone	6.85	+.370

The above results, which show a much lower oxidation potential in the buff sandstone than in the red sandstone, are consistent with the theory of origin outlined above and suggest that natural waters in equilibrium with the red and buff sandstones would have similar relative oxidation potentials. Although the Eh of the buff sandstone is not within the theoretical stability field of pitchblende, the samples of sandstone were taken from weathered outcrops and therefore the Eh values obtained from the buff sandstone may be considerably higher than those existing below the present zone of oxidation.

The lower oxidation potential in the buff sandstone is probably due in part to the larger ratio of ferrous iron to ferric iron in the buff sandstone than in the red sandstone. Carbonaceous material was not observed in the red and buff sandstone samples and therefore carbonaceous material is probably not responsible for the lower Eh in the buff sandstone.

Several experiments were conducted to determine the probable cause of environments sufficiently reducing to precipitate pitchblende in sediments. Samples of water-saturated carbonaceous material from the Fall River sandstone that were sealed in glass containers showed relatively high Eh values after a period of from 1 to 18 months. However, samples of water-saturated pyrite from the same carbonaceous material produced very low Eh values. The results are tabulated below:

	pH	Eh (volts)
Carbonaceous material with most of pyrite removed	4.1	0.436
Pyrite from above carbonaceous material	6.6	−0.040

These results, although preliminary, suggest that pyrite may be a primary control for the localization of uranium deposits and that the association of carbonaceous material with uranium deposits may be due to the reducing environment caused by pyrite contained in the carbonaceous material. It is of interest to note in the above table that the pH and Eh values for the water-saturated pyrite are within the theoretical stability field of pitchblende as determined by Garrels (3, p. 1017).

Although pyrite was not observed in specimens of carbonaceous material or sandstone from the Fall River sandstone in the area of investigation, pseudomorphs of goethite after pyrite were found in the basal unit of the Fall River sandstone, and abundant secondary gypsum, possibly derived from pyrite, is present in the weathered outcrops of carbonaceous beds. Abundant pyrite, probably of syngenetic origin, is present in unoxidized drill-core samples of Fall River sandstone from several areas in the northern Black Hills.

Several different geologic conditions may have been effective in producing a sufficiently reducing condition for the precipitation of pitchblende. Ground water moving downward along a permeable bed would become more reducing through oxidation of various elements with which it comes in contact. This usual change from oxidizing to reducing conditions would in many cases occur over a large area and therefore would not be effective in localizing and concentrating uranium deposits. Localization of the reducing environment, to produce concentrations of pitchblende, would be necessary and could be caused by structural features such as terraces or small domes. On these structures, if the permeable bed were not saturated, there might be a local decreased rate of flow which would allow time for the solution to reach equilibrium with pyrite or other ferrous iron minerals and to become sufficiently reducing to precipitate uranium. A continual flow of water through the rock would essentially dilute the reducing capacity of any reducing material present; but if the flow were hindered or stopped, an area could be formed, within which conditions were sufficiently reducing for the reduction of hexavalent uranium. Local thinning of the sandstone or decrease in permeability could also inhibit the flow of ground water. Uranium ions moving into such an environment would then be deposited as pitchblende. Concentrations of carbonaceous material, especially those containing abundant pyrite, could cause localized reducing conditions.

The information concerning the origin of the uranium occurrences in the area of this investigation is summarized below:

1. The uranium-bearing solutions are believed to have moved generally down dip.
2. Alteration of buff sandstone to red sandstone is believed to have been nearly contemporaneous with the uranium deposition and this suggests that primary uranium was deposited during the change of the solutions from oxidizing to reducing.
3. Laboratory evidence suggests that ground water in equilibrium with the red sandstone has a much higher oxidation potential than ground water in equilibrium with the buff sandstone.

4. Concentrations of primary uranium have resulted from localizations of reducing conditions. (Carnotite has formed by oxidation of the primary uranium during the present weathering cycle.)

5. Pyrite-bearing sandstone and pyritiferous carbonaceous material are effective in producing an environment sufficiently reducing for the precipitation of pitchblende.

6. Structures such as terraces or domes superimposed on the regional dip, local thinning or decrease in permeability, or concentrations of pyritiferous material may have been effective in localizing the reducing environment.

The evidence cited above justifies the conclusion that the uranium deposits have formed by the action of ground waters. However, the origin of the uranium in the ground water presents a separate problem and one which is closely related to the origin of the red altered sandstone.

ORIGIN OF THE RED ALTERATION

The red altered sandstone is probably the result of pre-Oligocene weathering. An altered zone below the base of the Oligocene has been recognized by several workers. Tourtelot (4, p. 80) states:

> Throughout large areas of the Great Plains in Nebraska and South Dakota, the predominantly shaly marine strata of Late Cretaceous age are overlain by tuffaceous sandstone and claystone of the Chadron formation at the base of the White River group of Oligocene age. A conspicuous feature of the unconformable contact between these two sequences is a brightly colored zone of altered Cretaceous shales beneath the Chadron.
>
> The zone is as much as 50 feet thick and is present everywhere except where channels were cut through it prior to the deposition of the Chadron formation. The altered shale ranges in color from nearly white through shades of yellow to orange, brown, and purple. Red streaks are common, and oxides of iron coat joints and bedding planes.

After detailed work on the weathered zone, Dunham (2, p. 8) found that the upper part of the weathered zone exhibits the chemical, mineralogical, and textural characteristics of a maturely developed soil.

Although rocks of White River age are not present in the immediate vicinity of the area of investigation, small outliers of pebble conglomerate, believed to be of White River age, rest unconformably on the Fall River sandstone in several localities in the northern Black Hills; in the area of investigation the pre-White River erosion surface was probably only about two hundred feet above the present bedrock surface. The red-buff contact may be the extension, down dip in the more permeable beds of the lowermost zone of a soil profile which was developed on pre-Oligocene strata.

Red alteration is not restricted to the Fall River sandstone in the northern Black Hills. For example, the Hulett sandstone member of the Upper Jurassic Sundance formation is also altered red for a considerable distance down-dip from the pre-White River erosion surface that was locally developed on the Hulett sandstone member on the north and west flanks of the Bear Lodge Mountains. The Bear Lodge Mountains are about 20 miles southwest of the area of investigation.

SOURCE OF THE URANIUM

The source of the uranium and associated elements is unknown. However, the author believes that these elements have been derived from dispersed sources in the sediments which have been eroded. Some of the uranium may have come from the altered part of the Fall River sandstone. There is no evidence to indicate that hydrothermal solutions have played a part in the origin of the uranium deposits. On the contrary, the available information concerning the behavior of uranium during weathering processes suggests that weathering of a slightly uraniferous rock coupled with a suitable reducing environment below can adequately account for the deposits.

ACKNOWLEDGMENTS

Laboratory space and equipment of the Geology Department of the University of Wisconsin were used for the preparation and study of rock samples. The use of these facilities is greatly appreciated.

The author is grateful for the very able assistance of Pierce D. Parker, U. S. Geological Survey, during the field work.

This work was done by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

1801 TABOR STREET,
DENVER 15, COLORADO,
March 14, 1957

REFERENCES

1. Bell, Henry, and Bales, W. E., 1955, Uranium deposits in Fall River County, South Dakota: U. S. Geol. Survey Bull. 1009-G, p. 211–231.
2. Dunham, R. J., 1955, Uranium minerals in Oligocene gypsum near Chadron, Dawes County, Nebraska: U. S. Geol. Survey TEI-525, issued by U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge.
3. Garrels, R. M., 1955, Some thermodynamic relations among the uranium oxides, and their relation to the oxidation states of the uranium ores of the Colorado Plateau: Am. Mineralogist, v. 40, p. 1004–1021.
4. Tourtelot, H. A., 1956, Radioactivity and uranium content of some Cretaceous shales, Central Great Plains: Am. Assoc. Petroleum Geologists Bull., v. 40, no. 1, p. 62–83.

THE PARAGENETIC RELATIONSHIPS OF GERMANITE AND RENIÉRITE FROM TSUMEB, SOUTH WEST AFRICA[1]

CHARLES B. SCLAR AND BRUNO H. GEIER

CONTENTS

PAGE

Abstract 612
Introduction 612
Mineralogical distribution of germanium in the hypogene sulfide ore 614
Possible equivalence of reniérite and "orange bornite" 614
Textural and genetic relationships of germanite and reniérite 621
Sequence of hypogene sulfide deposition and geochemical considerations 628
Acknowledgment 630
References cited 630

ABSTRACT

Germanium occurs as germanite and reniérite in the hypogene copper-lead-zinc ore body at Tsumeb, South West Africa. The principal hypogene sulfides that constitute the germanium-bearing ore are galena, tennantite, enargite, digenite, bornite, chalcopyrite, sphalerite, and pyrite. The two germanium-bearing sulfides are associated chiefly with galena, tennantite, and sphalerite and are mutually associated in large part on a microscopic scale.

Microtextural relationships show that germanite was one of the earliest minerals formed in the sequence of hypogene sulfide deposition and that reniérite was introduced later principally by replacement of the germanite and subordinately by replacement of the host rock. Replacement of germanite by an equal volume of reniérite requires an addition of iron and the corresponding removal of an approximately equivalent amount of germanium. The intimate association of early germanite and relatively late reniérite provides an example of the mineralogical redistribution of germanium induced by changing hypogene conditions.

X-ray and mineralographic data assembled from the literature support the hypothesis that some of the reported occurrences of "orange bornite" are actually occurrences of reniérite. In any exploration program for germanium, it would perhaps be expedient to re-examine those ores in which "orange bornite" is known to occur.

INTRODUCTION

THE Tsumeb mine in the northern part of the Otavi Mountains of South West Africa has been and will probably continue to be one of the greatest base-metal producers in the world. Within the last three years a greatly increased demand for germanium by the electronics industry has stimulated interest in the possibility of recovering germanium from the massive base-metal sulfide

[1] Presented before the Society of Economic Geologists, Annual Meeting, Los Angeles, 1954.

ores at Tsumeb in which significant amounts of this now valuable element are known to occur. This paper represents some of the results obtained through the efforts of the Tsumeb Corporation to determine the mineralogical and spacial distribution of the germanium in the Tsumeb ore body and to evaluate the concentratability of the germanium in the sulfide ore.

An excellent detailed account of the geology and ore deposits of the Tsumeb area is available in a paper by Schneiderhöhn (18), and an up-to-date résumé of the geologic setting of the Tsumeb mine was contributed recently by Söhnge (21). In brief, the ore body is a highly irregular but roughly pipe-shaped mass of sulfides that is localized in one limb of a syncline in a folded dolomite formation. In several discontinuous sections along its plunge, the ore body is not a solid mass of sulfidic ore but a shell of variable thickness, the core of which is a rock of controversial origin. The latter was considered to be a magmatic aplite by Schneiderhöhn (18) and has been called "pseudo-aplite" by Söhnge (21) who points out that there is evidence for a sedimentary origin as well. The ore minerals replace both the dolomite and the pseudo-aplite and appear to have been introduced principally by metasomatism. However, the position of the ore body within the dolomite strata appears to have been controlled by several local bedding-plane shear zones connected by oblique fractures. The Tsumeb ore body has been explored about 2,600 feet along its plunge and its lower limits have not yet been determined. In fact, according to Söhnge (21) the Tsumeb ore body attains its greatest known size on the 2,390-foot level where it is elliptical in horizontal projection with major and minor axes of 600 feet and 250 feet, respectively. The principal hypogene sulfide minerals are galena, sphalerite, tennantite, enargite, bornite, and digenite; subordinate hypogene sulfide minerals are pyrite, chalcopyrite, and germanite. Supergene sulfides are chalcocite and covellite. The oxidized zone is world renowned for its remarkable suite of secondary minerals of copper, lead, zinc, vanadium, and cadmium, many of which are either very rare or known only from Tsumeb.

The occurrence of germanium and its mineralogical expression as germanite in the sulfide zone of the copper-lead-zinc ore body at Tsumeb, South West Africa, has been known for about thirty years through the work of Schneiderhöhn (18), Pufahl (16), Kriesel (4, 5), and Thomson (22). In 1930, DeJong (1) investigated the crystal structure of germanite by X-ray diffraction methods, and several years later Moritz (10) completed a detailed paragenetic and spectrographic study of the sulfide minerals in the Tsumeb ore body between its surface exposure and the 1,375-foot level. Murdoch in 1953 (12) made an X-ray investigation of germanite, reniérite, and colusite, and showed that these minerals are essentially isostructural and probably pseudo-isometric.

Recent studies at the Tsumeb mine by Geier have disclosed the presence of a second germanium-bearing sulfide in the Tsumeb ore body. The purpose of this paper is to record some observations on the genetic relationships of the two known germanium-bearing sulfides in the Tsumeb mine, and their relative positions in the sequence of hypogene sulfide deposition.

The conclusions in this paper are based primarily on the results of detailed mineralogical studies of (1) a sample of germanium-rich ore from the 2,390-foot level of the Tsumeb mine, (2) a sample of the copper concentrate produced at the Tsumeb pilot-plant in April, 1952, and (3) magnetic fractions of this copper concentrate obtained with a Frantz Isodynamic Separator.

MINERALOGICAL DISTRIBUTION OF GERMANIUM IN THE HYPOGENE SULFIDE ORE

The mineral germanite is unique in that its only known occurrence is the Tsumeb mine. However, Geier has discovered that germanite is not the only germanium-bearing sulfide in the Tsumeb ore. On the 2,390-foot level of the Tsumeb mine, which is in the hypogene sulfide zone, he found microscopic grains of a distinctive copper-iron-germanium sulfide associated principally with galena, tennantite, germanite, and sphalerite and subordinately with bornite, chalcopyrite, chalcocite and pyrite. A few sporadic grains that could be recognized with a hand lens were observed, but none of these exceeded 1 mm in diameter. Germanium assays of this mineral range from 4.5 to 5.5 percent depending at least in part on the degree of contamination of the sample with either other sulfides and/or the carbonate host rock. Germanite, on the other hand, contains approximately $1\frac{1}{2}$ to $1\frac{3}{4}$ times as much germanium.

At first, Geier tentatively regarded this unknown germanium mineral as a new species which he designated "Mineral X," and Sclar tentatively correlated the mineral on the basis of its mineralographic properties with a poorly defined copper-iron sulfide known as "orange bornite" described by Murdoch (11, p. 64), Orcel (13), Merwin and Lombard (9), Harcourt (3, p. 105) and Ramdohr (17, p. 336). However, Murdoch (12) subsequently showed by means of X-ray analysis that the germanium mineral in question is essentially identical with reniérite, a copper-iron-germanium sulfide, which was formerly known only from the Prince Leopold mine at Kipushi, Belgian Congo. Chemical analyses of germanite and reniérite are assembled in Table 1. The mineralographic properties, mode of occurrence, and mineral associations of germanite, reniérite, and "orange bornite" from all reported occurrences known to the authors are summarized in Table 2. Detailed mineralographic data on germanite are available in standard reference works by Schneiderhöhn and Ramdohr (19); Short (20), and Uytenbogaardt (24). There is no description of germanite in the recent work by Ramdohr (17).

POSSIBLE EQUIVALENCE OF RENIÉRITE AND "ORANGE BORNITE"

Now that the equivalence of the second germanium-bearing sulfide in the Tsumeb ore and reniérite from the Belgian Congo has been established, it is of interest to review briefly the events that led to the recognition of reniérite as a mineral species. In 1928, Thoreau (23) described a magnetic mineral, which he called "orange bornite," in the sulfide ore from the Prince Leopold Mine at Kipushi. Several years later Legraye (7) re-examined the magnetic "orange bornite" of Thoreau and concluded that it was chalmersite (cubanite). Orcel (13) reported that reflectivity measurements on the "orange bornite" from Vaulry, France, do not support Legraye's correlation of "orange bornite"

with chalmersite, and stated that the "orange bornite" from Vaulry appears to have optical properties comparable with those of the synthetic compound Cu_5FeS_6 which was discovered by Merwin and Lombard (9). Additional mineralographic and textural data on the "orange bornite" in the ore from the Prince Leopold Mine were contributed by Masuy (8). Later, a restudy of the "orangite bornite" from the Prince Leopold Mine was made by Vaes (25) who analyzed the mineral and found that it contained approximately 7.7 per-

TABLE 1

CHEMICAL ANALYSES OF GERMANITE AND RENIÉRITE

	Germanite $[Cu_3(Fe,Ge,Zn,Ga)(S,As)_4]$				Reniérite $[(Cu,Fe)_3(Fe,Ge,Zn,Sn)(S,As)_4]$				
	1	2	3	4	5	6	7	8	9
Cu	42.12	45.39	45.40	39.44	41.63	41.35	41.10	42.05	41.18
Fe	7.80	4.56	7.22	10.70	13.73	13.84	13.73	13.78	12.80
Ge	10.19	8.70	6.20	7.04	7.75	6.80	6.80	6.37	5.46
Ga	1.85	0.76	—	—	—	—	tr.	—	0.52
Zn	3.93	2.58	2.61	3.56	3.53	3.53	3.70	3.94	—
Pb	0.96	0.66	0.69	0.26	tr.	tr.	tr.	tr.	2.15
Sn	—	—	—	—	—	—	0.16	—	—
As	1.37	4.13	5.03	4.86	0.87	0.95	1.00	0.79	4.95
S	31.27	30.65	31.34	31.44	31.51	31.83	31.68	31.69	30.48
SiO_2	—	0.23	0.75	1.68	—	—	—	—	1.96
Rem.	—	1.89	—	—	—	—	0.20	—	
Total	99.49	99.55	99.24	98.98	99.02	98.30	98.37	98.62	99.50

Chemical formulas for germanite and reniérite after Lambot (6); based on structural considerations and the four analyses of reniérite given by Vaes (25).

1. Germanite, Tsumeb, South West Africa. Klemm's analysis in Moritz (10). According to Murdoch (12), Moritz stated that the analyzed sample contained an estimated 20% of tennantite. Murdoch points out, however, that this is impossible because even if all the arsenic present is attributed to tennantite, it is equivalent to only 6.75% of tennantite. Murdoch also recalculated the analysis to account for this contamination. A study of Moritz's paper revealed that Moritz reported that the analyzed sample was obtained by carefully removing material from a polished surface under the microscope, although slight contamination with galena was recognized. Accordingly, it is concluded that Klemm's analysis is the one made on the purest material to date and that recasting the analysis to account for contamination by tennantite is not warranted. Probably, Murdoch meant to refer to the analysis of germanite by Pufahl (16)—analysis No. 3 of this paper—which was reportedly made on a sample contaminated with tennantite.

2. Germanite, Tsumeb, South West Africa. Kriesel's analysis in Kriesel (5) who states that the analysis was made on 50-gram samples which were probably contaminated with tennantite and pyrite. The remainder reportedly consists of 1.282% of Mo, 0.184% of WO_3, 0.122% of CaO, 0.136% of C, 0.071% of Cd, 0.055% of MgO, 0.02% of Mn, 0.013% of Co, 0.005% of Ag and Au, 0.004% of TiO_2, and 0.001% of Ni.

3. Germanite, Tsumeb, South West Africa. Pufahl's analysis in Pufahl (16) who reports that the analyzed sample was contaminated with about 20% of tennantite.

4. Germanite, Tsumeb, South West Africa. Todd's analysis in Thomson (22) who reports that the analyzed sample was contaminated with about 17% of pyrite and 5% of tennantite as determined by micrometric analysis of briquetted and polished grains.

5–8. Reniérite, Prince Leopold Mine, Kipushi, Belgian Congo. Bracq's analyses in Vaes (25) who reports that each analysis was made on a magnetic concentrate prepared from the minus 100-plus 200-mesh size fraction of each of four samples of ore obtained from different locations in the mine. The magnetic products were boiled in HCl to remove sphalerite and soluble gangue.

9. Reniérite, Tsumeb Mine, Tsumeb, South West Africa. Reiner's analysis in Murdoch (12). The analysis was reportedly made on material 90% pure. Galena was probably a major contaminant. The remainder consists of Mo, MgO, CaO, and SiO_2.

TABLE 2

MINERALOGRAPHIC AND PHYSICAL PROPERTIES, MODE OF OCCURRENCE, AND MINERAL ASSOCIATIONS OF GERMANITE, RENIÉRITE, AND "ORANGE BORNITE"

		Germanite, Tsumeb, South West Africa (1)	Reniérite, Tsumeb, South West Africa (2)	Reniérite, Kipushi, Belgian Congo (3)	"Orange bornite," Vaulry, France (4)	"Orange bornite," Morococha, Peru (5)	"Orange bornite," Cerro de Pasco, Peru (6)
Mineralographic and Physical Properties	Color (fresh surface)	Deep red	Bronze	Bronze			
	Color (polished section)	Deep rose to pinkish gray	Orange-brown	Orange-brown	Orange-brown	Orange	Yellow-orange
	Structure	Pseudo-isometric	Pseudo-isometric	Pseudo-isometric		Pseudo-cubic? (See text and Table 3)	
	Specific gravity	4.46 ±	4.5 ±	4.3 ±			
	Talmage hardness	C	C	C			
	Quality of polish	Very good	Very good	Very good			
	Polishing hardness	>galena, bornite; slightly <tennantite, <sphalerite	>galena, chalcopyrite; <tennantite, sphalerite	Slightly > chalcopyrite; <bornite			
	Hardness (Moh's)	4	4.5?	4.5			
	Cleavage	None	None	None	None		
	Reflectivity	Low	Moderate	Moderate	Moderate		
	Reflection pleochroism	None	Orange to brown	Orange to bronze with violet tint	Distinct		Distinct
	Optical behavior	Isotropic	Anisotropic	Strongly anisotropic	Strongly anisotropic	Strongly anisotropic	Strongly anisotropic
	Polarization colors	None	Yellow-brown to brown	Light yellow-brown to dark brown or grayish yellow to bluish gray	Bright yellow to yellow-brown	Brilliant	
	Twinning	None	Polysynthetic	Polysynthetic	Polysynthetic		Polysynthetic
	Etch reactions (Short's reagents)	Negative	HNO_3 slowly stains brown, fumes tarnish slightly; rest negative				HNO_3 negative; rest negative?
	Magnetism	Nonmagnetic	Strongly magnetic	Strongly magnetic			

TABLE 2.—(*Continued*)

	Germanite, Tsumeb, South West Africa (1)	Reniérite, Tsumeb, South West Africa (2)	Reniérite, Kipushi, Belgian Congo (3)	"Orange bornite," Vaulry, France (4)	"Orange bornite," Morococha, Peru (5)	"Orange bornite," Cerro de Pasco, Peru (6)
Mode of Occurrence	Minute single grains and granular aggregates disseminated through galena, tennantite, and host rock	Irregular patches, peripheral shells, and regular lamellae replacing germanite grains and irregular grains in host rock	Single grains and granular aggregates in hypogene sulfide ore; minute exsolution lamellae in chalcopyrite which disappear if heated in air at 1 atm to 550° C for 4 hours, chalcopyrite selectively replaced by bornite or chalcocite; 1.5 mm crystals with cubic forms on walls of cavities	Minute grains disseminated through bornite part of which is selectively replaced by chalcopyrite; intergranular networks in granular aggregates of "yellow stannite"	Irregular grains associated with chalcopyrite	Minute irregular inclusions in bornite
Mineral Associations	Galena, tennantite, sphalerite, and reniérite	Galena, tennantite, sphalerite, and germanite	Chalcopyrite, sphalerite, galena, bornite, tennantite, and chalcocite	Bornite, "yellow stannite," stannite, and chalcopyrite	Chalcopyrite, tetrahedrite, sphalerite, and enargite	Bornite, enargite, and digenite

Sources of data: (1) Schneiderhöhn and Ramdohr (19), Uytenbogaardt (24), Murdoch (12), and the authors. (2) Murdoch (12) and the authors. (3) Legraye (7), Masuy (8), and Vaes (25). (4) Orcel (13, 14). (5) Harcourt (3). (6) Orcel and Plaza (15).

cent germanium and 13.7 percent iron. Vaes concluded that the mineral should be accorded specific rank on the basis of its distinctive physical properties and chemical composition. Accordingly, he named it reniérite in honor of A. Renier, the Director of the Geological Survey of Belgium. Fleischer (2), in a review of Vaes' paper, expressed the view that this mineral should be considered a ferroan variety of germanite unless X-ray diffraction data disclose that it has a distinctive atomic structure. X-ray diffraction studies by Lambot (6) and Murdoch (12) subsequently supported Vaes' contention that reniérite is a definite mineral species.

Mineralographic characteristics of "orange bornite" from all reported occurrences closely resemble those of reniérite from the Belgian Congo and South West Africa (Table 2). Additional support for the tentative correlation of these minerals is forthcoming from a comparison of published X-ray diffraction data which are assembled in Table 3. Any discrepancies that exist between the interplanar spacings and line intensities of reniérite and "orange bornite" are probably within the limits of experimental error and/or anticipated variations in chemical composition of a complex mineral like reniérite. In regard to the latter possibility, it is perhaps significant that tin is reported

TABLE 3

COMPARISON OF X-RAY POWDER DIFFRACTION DATA FOR RENIÉRITE, "ORANGE BORNITE", AND PYRITE

Reniérite (1)			"Orange bornite" (2)		Pyrite (3)	
d/n	I	hkl	d	I	d	I
11.72	½	?				
10.25?	½	001				
8.96?	½	?				
7.50	1	011				
6.05	½	111				
5.30	½	002				
4.80	½	012				
4.31	2	112				
3.75	½	022	3.8			
3.55	½	003				
3.34	1	013	3.28	0.5		
3.06	10	222	3.08	6.0	3.10	0.5
2.96	½	023				
2.82	1	123	2.82B	1.0	2.76	3.0
2.65	3	004	2.68	1.0		
2.56	½	014				
2.50	½	033,114	2.49	1.0	2.46	3.0
2.386	½	024	2.38	1.0		
2.255	½	233	2.22	0.3	2.24	1.0
2.163	½	224				
2.13	½	005	2.11	0.2		
2.075	½	015,134				
2.03	½	115	1.965	0.3		
			1.930	0.3	1.93	2.0
1.87	8	044	1.890	4.0		
1.858	½	?				
1.816	½	035,334			1.82	0.5
1.722	½	116,235				

TABLE 3.—(*Continued*)

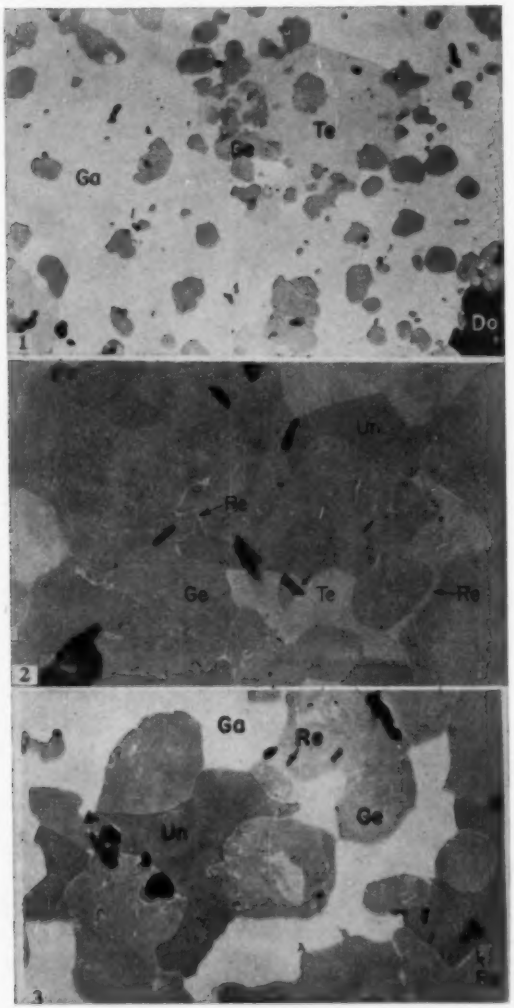
Reniérite (1)			"Orange bornite" (2)		Pyrite (3)	
d/n	I	hkl	d	I	d	I
			1.642	0.3	1.645	4.0
1.595	6	226	1.613	3.0	1.585	0.3
1.56	½	136				
1.529	1	444			1.522	0.5
1.497	½	017				
1.473	½	117,155			1.460	0.5
1.444	½	127,255,336				
1.435	½	?				
1.395	½	445,037,227				
1.325	1	008	1.337	1.0		
1.317		?				
			1.258	1.0	1.224	0.3
1.214	3	266				
1.194	½	048			1.195	0.3
					1.160	0.3
			1.114	0.3	1.120	0.3
1.083	2	?	1.093	1.0	1.050	1.0
1.080	1	448				
1.022	1	159,377	1.029	0.3	1.028	0.3
1.020	1	666,2.2.10				
1.016	½	0.3.10			1.013	0.3
					0.990	0.3
0.9395	½		0.946	0.2	0.961	0.5
0.9360	½					
0.9340	½					
0.8958B	½		0.904	0.2	0.907	0.5
					0.880	0.5
					0.825	0.5
					0.817	0.3
					0.807	0.3

(1) From Murdoch (12, Table 1). Average readings with Cu and Co radiation. Data are for reniérite from Prince Leopold Mine, Kipushi, Belgian Congo and Tsumeb Mine, Tsumeb, South West Africa. Indexing by Murdoch based on cubic unit cell with $a_0 = 10.583$Å.

(2) From Harcourt (3, p. 105). Cu radiation, nickel filter. Data are for "orange bornite," Harcourt's specimen No. 166, from Morococha, Peru.

(3) From Harcourt (3, p. 94). Cu radiation, nickel filter. Data are for pyrite, Harcourt's specimen No. 117, from Sudbury, Ontario. All the residual unmatched lines of spacing from comparison of reniérite with "orange bornite" can be matched with those of pyrite which is a major constituent of the Morococha ore.

by Harcourt to occur (3, p. 105) in the "orange bornite" from Morococha, Peru, although this element is reported in only one of the four analyses of reniérite from the Belgian Congo and is not reported in analyses of reniérite from South West Africa (Table 1). The "orange bornite" from Morococha, Peru, might possibly be a stanniferous variety of reniérite in which Sn^{+4} proxies for Fe^{+2}, and, in this respect, it is of interest to note the close association of "orange bornite" with cassiterite, stannite, and copper sulfides at Vaulry, France (14). The sample of "orange bornite" used by Harcourt to obtain an X-ray powder pattern appears to have been slightly contaminated with pyrite (Table 3), but the powder pattern, minus the lines apparently contributed by pyrite, corresponds closely to the powder pattern of germanite and even more closely to the powder pattern of colusite (cf. Murdoch, 12, Table 1).



Figs. 1 through 12—Photomicrographs of germanium-rich ore from the 2,390-foot level of the Tsumeb mine.

FIG. 1. Ovoids of germanite (Ge) disseminated through galena (Ga), tennantite (Te) and dolomite (Do). Note minute inclusions of an unidentified mineral in some of the germanite ovoids. × 120.

FIG. 2. Grains of germanite (Ge) and the unidentified mineral (Un) in a matrix of tennantite (Te). The roughened appearance of the grain of the unidentified mineral (right center) is due to minute unreplaced remnants of sphalerite.

This is probably a direct reflection of the isostructural relationships of colusite, germanite, and reniérite, which Murdoch recently determined.

The significance of these developments from the standpoint of the economic geologist is the possibility that other reported occurrences of "orange bornite" are actually occurrences of reniérite. As examples, the "orange bornite" in the copper ore from the San Expedito Mine, Cerro de Pasco, Peru, described by Orcel and Plaza (15, p. 230, Pl. 11, Fig. 1), the "orange bornite" in the copper ores of Morococha, Peru, recorded by Harcourt (3, p. 105, 112), and the "orange bornite" in the tin-bearing ores of Vaulry, France, reported by Orcel (14), might well be re-examined with this concept in mind. In any event, it would perhaps be expedient to re-examine those ores in which "orange bornite" is known to occur when an exploration program for germanium is undertaken.

TEXTURAL AND GENETIC RELATIONSHIPS OF GERMANITE AND RENIÉRITE

The germanium-bearing sulfide ore at Tsumeb is composed principally of massive granular aggregates of galena, tennantite, enargite, digenite, bornite, chalcopyrite, sphalerite, and pyrite, which are enclosed in a host rock of cherty dolomite. Germanite and reniérite appear to occur in approximately equal amounts. They are associated principally with galena and tennantite, and to a lesser degree with sphalerite. Both germanium minerals are also disseminated through the host rock, and, as will be shown in the succeeding discussion, the germanium minerals are mutually associated in large part.

Germanite almost invariably occurs as microscopic grains and granular aggregates. However, in rare occurrences, germanite is visible to the unaided eye as irregular patches with a metallic luster and a deep red tint enclosed in massive aggregates of galena and/or tennantite or enclosed in the host rock. Most of the germanite has a characteristic microtextural relationship to the sulfides associated with it. The mineral occurs as ovoid "islands" or chains of ovoid "islands" disseminated through a "sea" composed of granular aggregates of tennantite and/or galena (Fig. 1). In places, veinlets of the matrix (tennantite or galena) crosscut and replace the germanite ovoids (Figs. 4, 6). The germanite ovoids range in size from about 10 microns to 75 microns; the average size is about 30 microns. A subordinate amount of germanite occurs as irregular grains, which range in size from 5 to 30 microns, disseminated through the host rock. Some of the germanite ovoids show a distinct zonation or mottling (Figs. 2, 3, 4, 5) which is due to a color variant of germanite. This color variant is paler and grayer than the more voluminous rose-colored germanite, but it has about the same polishing hardness and optical behavior.

Note inclusions of the unidentified mineral in germanite, some of which are surrounded by a border of reniérite. Reniérite (Re) also occurs along germanite grain boundaries. Note pale color variant of germanite as core of germanite grain (lower center). × 550.

FIG. 3. Grains of germanite (Ge) and the unidentified mineral (Un) in galena (Ga). Note pale color variant of germanite in zoned germanite grain (center). Reniérite (Re) occurs along germanite grain boundaries and as borders around inclusions of the unidentified mineral in germanite. × 550.

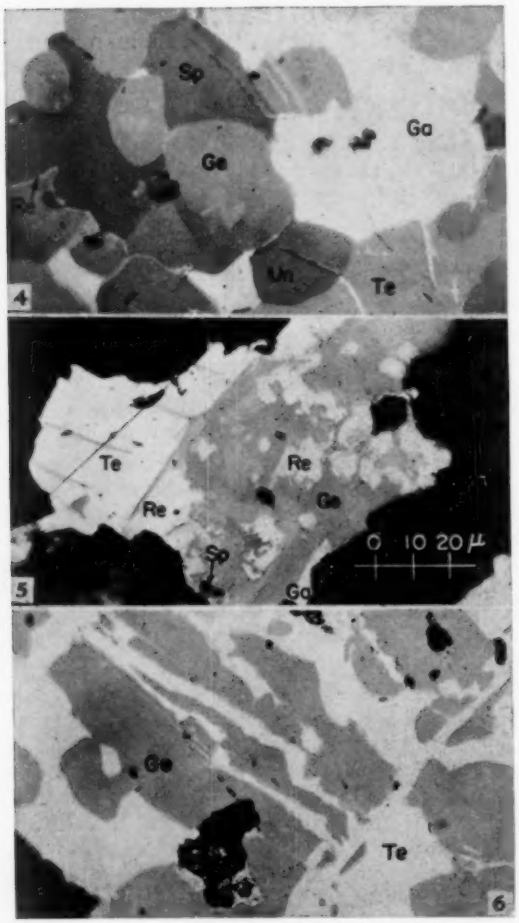


FIG. 4. Grains of germanite (Ge), sphalerite (Sp), and the unidentified mineral (Un) in galena (Ga) and tennantite (Te). Reniérite (Re) rims some of the germanite grains. Note oriented replacement lamellae of the unidentified mineral in sphalerite (left center) and veinlets of galena that cut germanite and tennantite. Also note patches of pale color variant of germanite in germanite grains (center and left center). × 500.

FIG. 5. A particle of ore mounted in Lucite. The particle is composed principally of tennantite (Te) and germanite (Ge). Mottled appearance of germanite due partly to irregular areas of a pale color variant of germanite and partly to brighter irregular patches of reniérite (Re). Note inclusion of sphalerite (Sp) and area of galena (Ga). × 600.

FIG. 6. Veinlets of tennantite (Te) cutting through and replacing germanite (Ge) grains. (Do) is dolomite. × 320.

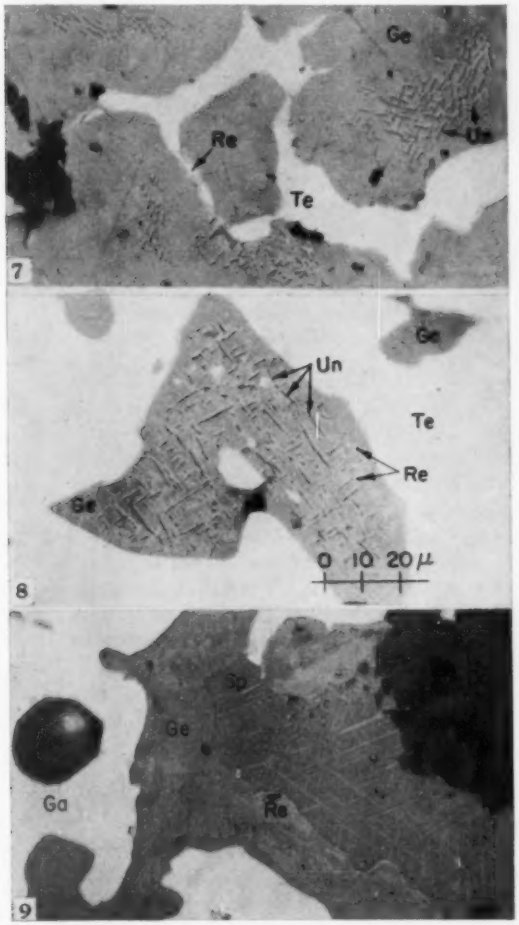


FIG. 7. Grains of germanite (Ge), some of which have oriented inclusions of the unidentified mineral (Un), in a matrix of tennantite (Te). Reniérite occurs along several germanite grain boundaries. × 560.

FIG. 8. Grains of germanite (Ge), one of which contains numerous oriented inclusions of the unidentified mineral (Un), in a matrix of tennantite (Te). Many of the inclusions are surrounded by a border of reniérite (Re). × 600.

FIG. 9. Sphalerite (Sp) with replacement lamellae of the unidentified mineral along its cubic or octahedral planes, and an irregular area of germanite (Ge) mottled by irregular patches of reniérite (Re). The matrix is galena (Ga) and dolomite (Do). × 320.

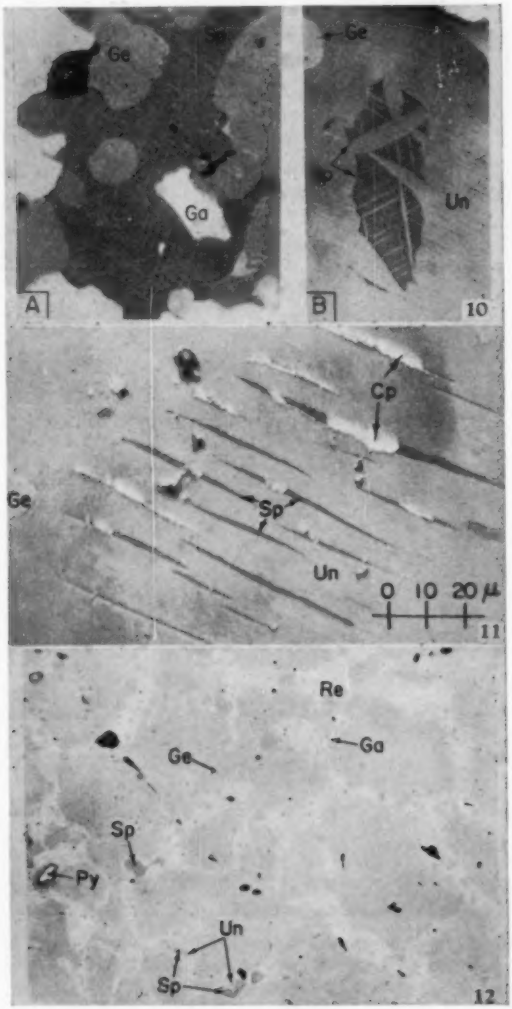


FIG. 10a. Sphalerite (Sp) with replacement lamellae of the unidentified mineral along its cubic or octahedral planes associated with grains of germanite (Ge) and galena (Ga). × 570.

FIG. 10b. Unreplaced remnants of sphalerite (Sp) enclosed in the unidentified mineral (Un) which has developed in part along the cubic or octahedral planes of the sphalerite. Note the associated grain of germanite (Ge). × 550.

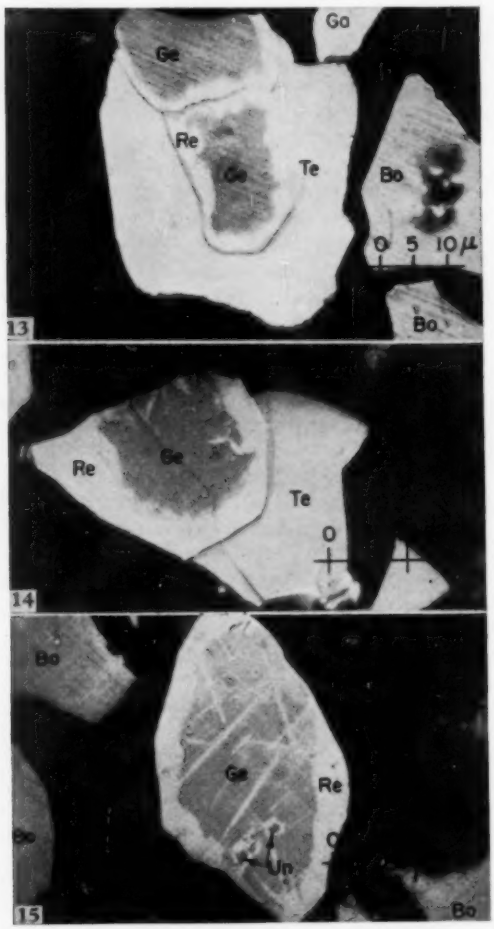
FIG. 11. Oriented residual lamellae of sphalerite (Sp) in the unidentified mineral (Un). The sphalerite lamellae have been selectively replaced in part by chalcopyrite? (Cp). (Ge) is germanite. × 600.

It occurs as irregular cores in germanite ovoids, irregular patches commonly near the centers of germanite ovoids, and as concentric spherical shells within germanite ovoids. One specimen of the ore contained some irregular germanite grains of unusual color enclosed in reniérite. Some of these germanite grains are composed wholly of the pale color variant of germanite. Others are zoned grains in which the cores are a darker bluish gray and the peripheral zones are apparently equivalent to the color variant of germanite.

Some of the germanite ovoids contain minute rod-shaped to anhedral inclusions of an unidentified gray isotropic mineral (Figs. 7, 8) that is distinctly harder than germanite. Essentially all the inclusions are less than ten microns long and five microns wide, but the volume ratio of inclusions to germanite host, although variable, may be as high as 2 to 3 in some germanite ovoids. The rod-shaped inclusions are commonly oriented along the cubic or octahedral planes of the germanite host (Figs. 7, 8); the anhedral inclusions are either randomly dispersed in the germanite or show a subgraphic arrangement with respect to the germanite (Fig. 2). Both the rod-shaped oriented inclusions and the anhedral unoriented inclusions are considered to be of replacement origin. The inclusions are nonuniformly distributed with respect to groups of germanite ovoids as well as within single germanite ovoids. As a result, adjoining germanite ovoids may be either devoid of or crowded with inclusions (Fig. 8), and individual germanite ovoids may have both homogeneous and heterogeneous patches (Fig. 7). The mineral that constitutes the inclusions is probably equivalent to Moritz's (10, p. 123) "Unidentified Mineral No. IV." Moritz reports that a spectrographic analysis of a sample of this mineral, which perforce contained germanite as a contaminant, showed a notably strong line for lead as compared with germanite. However, no additional elements, other than those that constitute germanite, were detected.

In addition to its occurrence as minute inclusions in germanite grains, the unidentified mineral occurs as discrete grains in granular aggregates of germanite, galena, tennantite, and sphalerite (Figs. 2, 3, 4) and as lamellae of replacement origin along the cubic or octahedral planes of sphalerite (Figs. 9, 10). Grains in which replacement of sphalerite by the unidentified mineral has progressed almost to completion commonly consist of oriented remnants of sphalerite in a matrix of the unidentified mineral (Fig. 11). Some of these residual inclusions of sphalerite have been selectively replaced in part by a mineral that appears to be chalcopyrite (Fig. 11). Even at a magnification of 600 diameters, some of the discrete grains of the unidentified mineral appear to have a "roughened" surface (Fig. 2). Higher magnifications reveal that this conditions is due to exceedingly minute unreplaced remnants of sphalerite in the unidentified mineral. Moritz (10) pointed out that the unidentified mineral is very similar in appearance to sphalerite and is difficult to distinguish from sphalerite unless both minerals are present in the same field, although an oil-immersion objective will enhance the slight difference in re-

FIG. 12. Grains of germanite (Ge) partly replaced by an intergranular network of reniérite (Re). Note grains of sphalerite (Sp) and the associated unidentified mineral (Un), a grain of pyrite (Py), and a veinlet of galena (Ga), × 300.



Figs. 13 through 17—Photomicrographs of a magnetic fraction of a copper concentrate obtained with a Frantz isodynamic separator.

FIG. 13. Ore particles mounted in Lucite. The composite particle is made up of two germanite (Ge) grains which are partly replaced by reniérite (Re) along grain boundaries; the matrix is tennantite (Te). Adjoining particles are bornite (Bo) and galena (Ga). × 1,150.

FIG. 14. Ore particles mounted in Lucite. Composite particle made up of germanite (Ge) partly replaced by reniérite (Re) and of tennantite (Te). × 1,250.

FIG. 15. Ore particles mounted in Lucite. A grain of germanite (Ge) partly replaced by a shell of reniérite (Re) from which lamellae have developed along the cubic or octahedral planes of the germanite. Note inclusions of the unidentified mineral (Un) in the germanite. Adjoining particles are bornite (Bo). × 1,250.

flectivity between the two. This observation was verified during the course of this study. Although the unidentified mineral is of interest because of its association with the germanium minerals, it is a very minor constituent of the ore as a whole.

Reniérite was observed to occur in the following characteristic and genetically significant microtextural relationships:

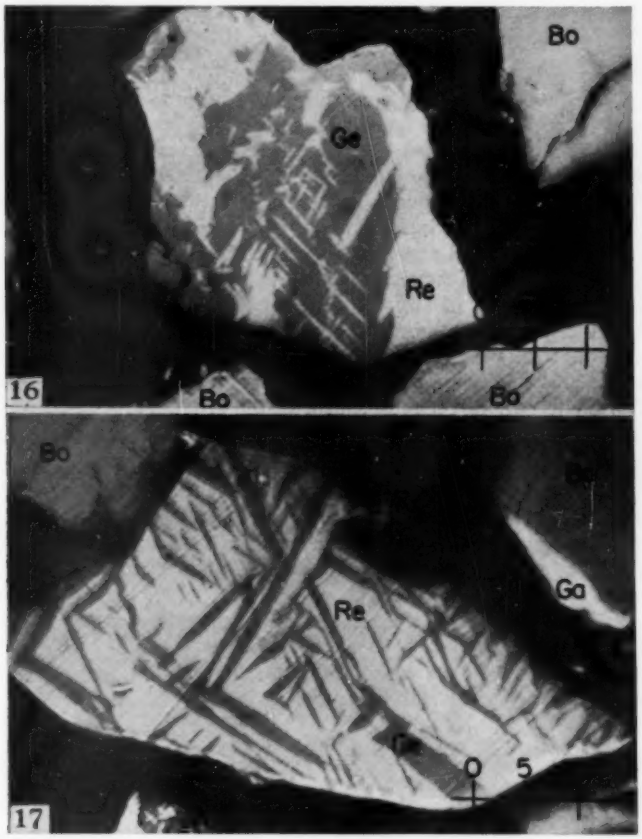


FIG. 16. Ore particles mounted in Lucite. A particle composed of germanite (Ge) partly replaced by reniérite (Re) which has developed in part along the cubic or octahedral planes of the germanite. Adjoining particles are bornite (Bo). × 1,560.

FIG. 17. Ore particles mounted in Lucite. A particle composed of reniérite (Re) and residual unreplaced lamellae of germanite (Ge). The adjoining particles are composed of bornite (Bo) and galena (Ga). × 1,560.

(1) Continuous and discontinuous shells of variable thickness around germanite ovoids and as intergranular networks in aggregates of germanite grains (Figs. 2, 3, 4, 7, 12, 13, 14).

(2) Shells of variable thickness around the inclusions of the unidentified mineral in germanite (Figs. 2, 3, 8).

(3) Irregular patches within germanite grains (Figs. 5, 9).

(4) Lamellae of variable thickness developed along the cubic or octahedral planes of germanite so as to form a regular intergrowth with that mineral (Figs. 14, 15, 16, 17).

(5) Irregular grains disseminated through the host rock.

As is evident from the photomicrographs, all stages of the replacement of germanite by reniérite, from incipient to essentially complete, were observed. The hypogene solutions responsible for this replacement penetrated along the grain boundaries between germanite grains, along the grain boundaries between germanite and contiguous minerals, and along the grain boundaries between germanite and inclusions of the unidentified mineral. The textures that resulted from partial replacement of germanite by reniérite range from highly regular, in which certain crystallographic planes in the germanite host guided the development of the reniérite, to unsystematic, in which directional control of the growth of the metasome by the host is not apparent. These microtextural relationships of reniérite demonstrate that it was introduced into the ore principally by selective replacement of the pre-existing germanite and subordinately by direct replacement of the host rock of cherty dolomite.

SEQUENCE OF HYPOGENE SULFIDE DEPOSITION AND GEOCHEMICAL CONSIDERATIONS

Textural evidence presented in the preceding section of this paper has shown that germanite was formed earlier than reniérite in the sequence of hypogene sulfide deposition. There remains for discussion the relative positions of the two germanium minerals with respect to the hypogene base-metal mineralization and the geochemical aspects of the transformation of germanite to reniérite.

The sequence of deposition of the hypogene sulfides that constitute the germanium-bearing base-metal ore is as follows:

1. Pyrite
2. Germanite, Bornite, Enargite
3. Sphalerite
4. Tennantite
5. Unidentified mineral, Chalcopyrite
6. Reniérite
7. Digenite,* Galena

* The exact position of digenite in the sequence of hypogene sulfide mineralization at Tsumeb is currently being investigated by Geier. Schneiderhöhn (18) and Moritz (10) concluded that the digenite is younger than the galena, but Geier's studies indicate that most of the galena was introduced after the digenite. Digenite was not observed in the germanium-rich ore from the 2,390-foot level of the Tsumeb mine, but, with respect to the germanium minerals in the copper concentrate which was produced in the Tsumeb pilot plant in April, 1952, digenite is clearly younger than germanite and is probably either younger than or contemporaneous with reniérite.

This paragenetic sequence is based solely on the authors' interpretation of microtextures observed in the germanium-rich ore from the 2,390-foot level of the Tsumeb mine and in the copper concentrate produced in the Tsumeb pilot plant in April, 1952. As a consequence, it is considered to be of limited validity with respect to the base-metal hypogene sulfides in the Tsumeb ore body as a whole, although this sequence is essentially in accord with the earlier conclusions of Schneiderhöhn (18) and Moritz (10). Geier has been engaged in a detailed study of the paragenesis of the base-metal sulfides in the deposit, and the results of his investigations to date show that the sequence of base-metal mineralization is much more complicated than has been previously indicated. There is evidence, for example, of two generations of chalcopyrite and, possibly, of two generations of galena. Nevertheless, the paragenetic relationships of the germanium minerals to each other and to their associated sulfides, as discussed in this paper, are probably valid for a much larger portion of the hypogene sulfide body at Tsumeb than is actually represented by the materials upon which this study is based.

In regard to the paragenesis of the two germanium sulfides, it is noteworthy that germanite is one of the oldest minerals and that reniérite is one of the younger minerals in the sequence. Also of interest are the successive compositional changes in the hypogene solutions during the period of metallization which are indicated by the mineral sequence; viz., iron, copper-iron-germanium, zinc, copper, copper-iron-germanium, and copper-lead.

The genetic relationships of the germanite and reniérite in the Tsumeb ore pose an interesting geochemical problem; namely, the replacement of a germanium-bearing sulfide containing approximately 10 percent germanium and 8 percent iron by an isostructural strongly magnetic germanium-bearing sulfide which contains approximately 6 percent germanium and 13 percent iron. If chemical analyses No. 1 and No. 9 in Table 1 are recalculated to 100 percent, the weights of the elements in 1 cubic centimeter each of germanite (Sp. Gr. = 4.46) and of reniérite (Sp. Gr. = 4.3) are as follows:

	Germanite	Reniérite	Difference
Cu	1.89 gms.	1.82 gms.	
Fe	.35	.56	+.21 gms.
Ge	.46	.24	−.22 gms.
Ga	.08	.02	
Zn	.18	—	
Pb	.04	.10	
As	.06	.22	
S	1.40	1.34	
	4.46 gms.	4.30 gms.	

Therefore, replacement of germanite by an equal volume of reniérite requires an addition of iron and the corresponding removal of an approximately equivalent amount of germanium. These figures also show that if germanite is replaced by reniérite, there is enough germanium released as a result of the transformation to produce about 1.8 times as much by weight of reniérite as compared with the weight of the germanite replaced, providing, of course, that the other elements that are essential constituents of reniérite are available. Inasmuch as all quantitative data obtained to date on the relative amounts of

germanite and reniérite in the ore indicate that these minerals are present in approximately equal proportions, it appears unlikely that any germanium was introduced into the ore body at the time the reniérite was formed. Rather, it appears that the partial conversion of germanite to reniérite is a record of the mineralogical redistribution of germanium induced by changing hypogene conditions.

ACKNOWLEDGMENT

The authors are indebted to the officials of the Tsumeb Corporation for permission to publish this paper. The original data included in this paper were acquired at Tsumeb by B. H. Geier and at Battelle by C. B. Sclar during the course of a research and development program sponsored by the Tsumeb Corporation. We also wish to acknowledge the material aid of Battelle Memorial Institute in the preparation of this paper for publication.

The authors wish to thank M. D. Banghart of the Tsumeb Corporation and Newmont Mining Corporation and O. F. Tangel of the Battelle Memorial Institute for arrangements made in connection with publication.

BATTELLE MEMORIAL INSTITUTE,
COLUMBUS, OHIO,
TSUMEB CORPORATION LIMITED,
TSUMEB, SOUTH WEST AFRICA,
March 6, 1957

REFERENCES CITED

1. De Jong, W. F., 1930, Die Kristallstruktur von Germanit: Zeitschr. Kristallographie, v. 73, p. 176–180.
2. Fleischer, M., 1950, Discredited minerals: renierite: Am. Mineralogist, v. 35, p. 136.
3. Harcourt, G. A., 1942, Tables for the identification of ore minerals by x-ray powder patterns: Am. Mineralogist, v. 27, p. 63–113.
4. Kriesel, F. W., 1923, Gallium im Germanit von Tsumeb: Metall u. Erz, v. 20, p. 257–259.
5. ——, 1924, Über die Analyse des neuen Germanium-Gallium-Minerals "Germanit": Chem.-Zeitung, v. 48, p. 961–963.
6. Lambot, H., 1950, Sur la reniérite: Annales soc. géol. Belgique, t. 73, p. 183–186.
7. Legraye, M., 1933, Un sulfure double de cuivre et de fer particulier des minerais de cuivre du Katanga: bornite orange ou chalmersite(?): Acad. roy. sci. Belgique Mém., sér. 5, t. 19, p. 262–268.
8. Masuy, G., 1938, Étude des minerais de cuivre du gisement Prince Léopold (Kipushi) de l'U.M.H.K., Com. spécial Katanga Annales, t. 9, p. 50–73.
9. Merwin, H. E., and Lombard, R. H., 1937, The system Cu-Fe-S: ECON. GEOL., v. 32, p. 203–284.
10. Moritz, H., 1933, Die sulfidischen Erze der Tsumeb Mine vom Ausgehenden bis zur XVI Sohle (–460 m.), Neues Jahrb., Beilage-Band 67A, p. 118–153.
11. Murdoch, J., 1916, Microscopical Determination of the Opaque Minerals: McGraw-Hill, New York.
12. ——, 1953, X-ray investigation of colusite, germanite, and reniérite: Am. Mineralogist, v. 38, p. 794–801.
13. Orcel, J., 1937, Sur l'existence de l'érubescite orange et d'un nouveau sulfure double de cuivre et de fer dans l'érubescite de Vaulry (Haute-Vienne): Compt. Rend. 70e Congr. Soc. Savantes, v. 26, p. 135–139.
14. ——, 1943, Composition minéralogique et structure des zones cuprifères du minerai stannifère de Vaulry (Haute-Vienne): Soc. franç. minéralogie, Bull. 66, p. 435–461.
15. ——, and Plaza, G., 1928, Étude microscopique de quelques minerais métalliques du Pérou: Soc. franç. minéralogie, Bull. 51, p. 230.
16. Pufahl, O., 1922, "Germanit" ein Germanium-Mineral und -Erz von Tsumeb, Südwest-Afrika: Metall u. Erz, v. 19, p. 324–325.

17. Ramdohr, P., 1950, Die Erzmineralien und ihre Verwachsungen: Akad. Verlag, Berlin.
18. Schneiderhöhn, H., 1920–1921, Die Erzlagerstätten des Otaviberglandes, Deutsch-Südwestafrika: Metall u. Erz, v. 17, p. 293–302, 361–368, 421–428, 544–551; v. 18, p. 22, 225–236, 266–272.
19. ——, and Ramdohr, P., 1931, Lehrbuch der Erzmikroskopie, Band II: Gebrüder Borntraeger, Berlin.
20. Short, M. N., 1948, Microscopic determination of the ore minerals, second edition: U. S. Geol. Survey, Bull. 914.
21. Söhnge, G., 1952, Massive-sulfide ore body at Tsumeb, South West Africa: Mining World, v. 14, p. 22–25.
22. Thomson, E., 1924, A mineralographic study of germanite: Toronto Univ. Studies, Geol. ser. 17, p. 62–65.
23. Thoreau, J., 1928, Le gisement Prince Léopold, Kipushi, Katanga: Louvain Univ., Inst. géol., Mém., t. 4, fasc. 3, p. 273.
24. Uytenbogaardt, W., 1951, Tables for microscopic identification of ore minerals: Princeton University Press.
25. Vaes, J. F., 1948, La reniérite (anciennement appelée "bornite orange"). Un sulfure germanifère provenant de la Mine Prince-Léopold, Kipushi (Congo belge): Annales soc. géol. Belgique, t. 72, p. 19–32.

ANHYDRITE COMPLEX OF THE MOROCOCHA DISTRICT, PERU[1]

R. H. NAGELL

CONTENTS

	PAGE
Abstract	632
Introduction	632
Acknowledgments	634
Geological setting	634
Limestone alteration types	634
Ores	636
Anhydrite complex	636
Distribution	637
Composition	637
Theories of origin	639
Origin of the collapse breccias	642
Conclusions	643
References	643

ABSTRACT

The Morococha mining district in central Peru is a source of copper-silver-lead-zinc ores. Jurassic limestones, intruded by Tertiary quartz monzonite stocks, are altered to rocks containing diopside-tremolite, serpentine-chlorite-talc, and anhydrite.

Diverse opinions regarding the origin of the anhydrite and associated breccia zones at Morococha have been published. The theories of origin may be grouped as hydrothermal replacement of limestone and syngenetic with the limestone. Hydrothermal replacement of the Jurassic Potosi limestone, following intrusion of the quartz monzonite stocks and prior to ore deposition, fits the facts best.

After emplacement of the ore bodies, descending meteoric waters converted the upper part of the anhydrite complex to gypsum. Some of the gypsum was taken into solution. Brecciation resulted from collapse of the solution cavities.

INTRODUCTION

THE Morococha mining district in central Peru (Fig. 1) yields copper-silver-lead-zinc ores from mesothermal deposits associated with Tertiary intrusives. The writer became familiar with these deposits during three years of residence at Morococha.

Hypogene anhydrite has been reported in mining districts by: Bowditch (2), Boyle (3), Butler (4), Collins (7), James (10), and Langford and Hancox (12). The deposits for the most part are fissure filings associated with copper

[1] Published with the permission of the Cerro de Pasco Corporation.

or gold ores. At the Potrerillos Mine, Chile, Sales (16) describes a porphyry plug intruding slightly folded limestone with "large amounts of massive anhydrite" of hypogene origin apparently replacing limestone at depth.

Some 100,000,000 tons of calcium sulfate in the form of gypsum and anhydrite are present at Morococha. The anhydrite is of interest inasmuch as widely divergent opinions regarding its origin have been published. The anhydrite at Morococha is described by Moore (14, p. 99) as related to replacement of limestone by late hydrothermal activity associated with ore deposition. Schmedeman (17, p. 678) states that, "It (the anhydrite) is probably related in age and origin to the contact metamorphic alterations, which it exceeds in

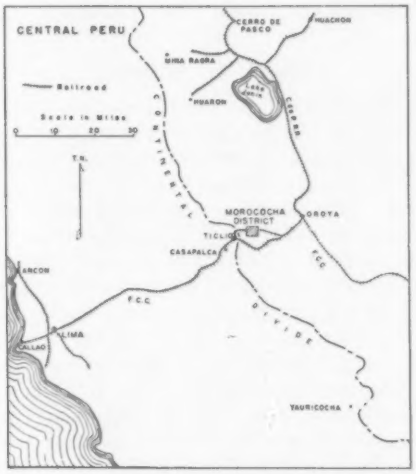


FIG. 1. Map of central Peru showing the location of the Morococha District.

magnitude." Mark, Faulkner, and Graton (13, p. 239) consider the anhydrite-gypsum to represent "hydrothermal outliers of the pyrometasomatic inner zone." Haapala (9, p. 21) believes that the anhydrite is of sedimentary origin.

Disagreement is also evident regarding the origin of certain breccias associated with the anhydrite complex. The term collapse breccias has been applied to distinguish them from other tectonic breccias present. Schmedeman (17, p. 678) ascribes their origin to collapse of cavities formed by solution of anhydrite by hydrothermal fluids with some solution by supergene waters. He believes that, "On the whole however, the breccias are closely related spatially to the ore zones and appear to be related in age and origin thereto." Mark, Faulkner, and Graton (13, p. 240) state that, "But where a tongue (quartz monzonite) penetrated into or reached almost up to a mass of anhydrite-gypsum, the solutions were able to dissolve important quantities of this sulfate material, producing thereby solution caves of various sizes, shapes and atti-

tudes." A footnote (op. cit.) states, "There are other evidences besides direct association with small quartz monzonite masses, that these caves are not the work of the normal vadose circulation, present or past." The evidence, however, is not presented in the paper cited.

The problem, then, concerns a rather large unusual occurrence of anhydrite with uncertainties as to its origin and position in the sequence of geologic events. Similarly the time, space and origin of brecciation of this rock require clarification.

Acknowledgments.—Drs. C. F. Park, F. L. Humphrey, and K. B. Krauskopf of Stanford University and Mr. H. L. Hosmer of the Cerro de Pasco Corporation have kindly read and criticized the manuscript. The writer, however, assumes responsibility for the views expressed.

GEOLOGICAL SETTING

The Morococha district is on the nose of the north plunging Yauli anticline. A thick "basement" of Carboniferous volcanic flows and tuffs known locally as the Catalina volcanics is overlain in general conformity by the Jurassic Potosi formation which is 1,500 feet thick and normally consists of limestones and dolomites. The overlying Cretaceous Santo Toribio formation, consisting of sandstones and intercalated basalts, has been removed by erosion from the crest of the anticline. During the Tertiary period these rocks were intruded by the Anticona quartz diorite to the west and by quartz monzonite stocks along the axis of the fold and to the east. The Potosi, San Francisco, and Gertrudis are the three major quartz monzonite stocks. The intrusives range in composition from quartz diorite through grandodiorite to quartz monzonite according to analyses presented by Lacy (11, p. 125). The Potosi and San Francisco stocks are larger than the Gertrudis (Fig. 2) and are considered to have followed the intrusion of the Anticona quartz diorite. The Gertrudis stock, because of its lack of through-going vein structures, probably represents the final phase of igneous and tectonic activity.

Limestone Alteration Types.—Attendant upon intrusion of the quartz monzonite stocks was the alteration of the Potosi limestone to marble, silicated "limestone," hydrated "limestone," and anhydrite.

The marble occurs toward the periphery of the district away from the intrusives. Unaltered carbonate rock is not found adjacent to intrusives.

Silicated "limestone" is a local term used to designate the alteration type characterized by the minerals diopside and tremolite which constitute the bulk of the rock. Toward its outer margin the silicated "limestone" is interbedded with the marble. Its distribution is probably determined in part by the presence of dolomitic layers in the limestone and in part by differences in permeability of the limestone. Toward the center of the district, the silicated "limestone" becomes dominant and may persist up to intrusive contacts. More commonly, however, it gives way to hydrated "limestone," especially near the San Francisco stock (Fig. 2). Most of the silicated "limestone" is a fine mosaic of diopside with tremolite. Garnet and epidote are locally abundant. Vesuvianite, scapolite, and wollastonite are rare.

The hydrated "limestone" contains no remanent carbonate. In contrast to the hard, white, blocky silicated "limestone," it is soft and green because of its characteristic serpentine and/or chlorite-talc composition. The distribution of the hydrated "limestone" is closely related to intrusives, especially the San Francisco stock. Its halo-like distribution is interrupted by interfingering layers of silicated "limestone." The hydrated type of alteration was extended toward the periphery of the district by hydrothermal ore solutions. Vein structures in the silicated "limestone" are bounded by narrow zones of chlorite and talc. Magnetite with ludwigite and chrysotile are locally abundant near intrusives, and disseminated pyrite is common throughout.

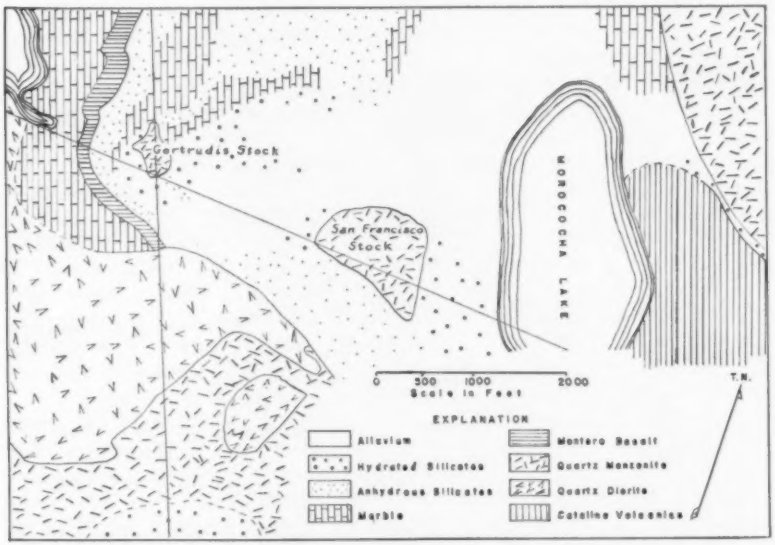


FIG. 2. Geologic sketch map of Morococha showing location of vertical sections.

The marmoritization and silication accompanied by probable magnesium metasomatism of the limestone preceded and was contemporaneous with intrusion of the San Francisco stock and its satellitic dikes. Alteration of the silicated "limestone" to hydrated minerals of serpentine, chlorite, and talc, with introduction of pyrite, was accomplished by hydrothermal activity associated with this stock and with later ore mineralization. The distribution of these alteration types follows a halo-like pattern surrounding the intrusives with superimposition of a layered pattern conforming to the attitude of bedding in the Potosi formation away from the intrusive contacts. Much of the work done in bringing order to the distribution of limestone alteration at Morococha was by Haapala and is contained in a private report to the Cerro de Pasco Corporation (1953).

Ores.—Ore mineralization followed cessation of intrusive activity and alteration of the limestone. Orebody types at Morococha are veins, contact pipes, and mantos. East-west vein structures are found in all rock types except the anhydrite and Gertrudis stock. Contact pipes are generally in contact with quartz monzonite intrusives. The contact pipes associated with the San Francisco stock are localized where veins in the stock intersect the contact. No veins exist in the Gertrudis stock or in the enclosing anhydrite. The pipes adhere strictly to the Gertrudis stock contact, which was the channel for ascent of ore solutions. Mantos in the form of gently inclined pipes

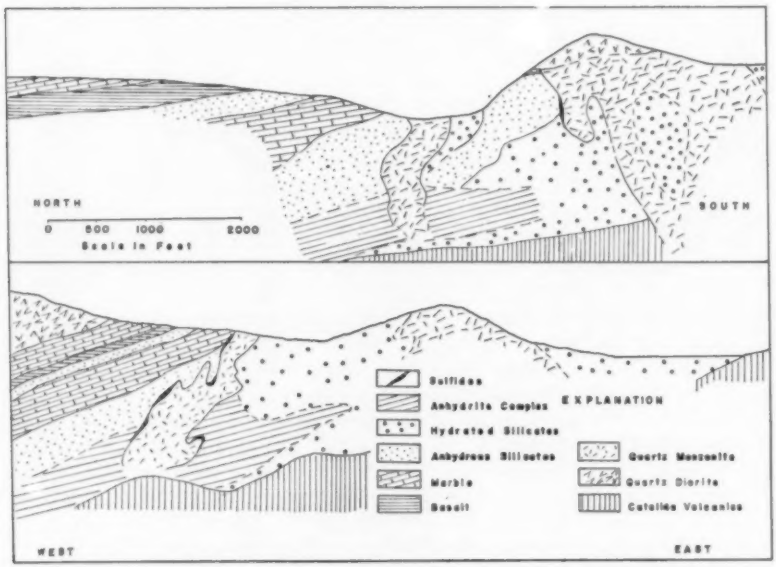


FIG. 3. Vertical sections through the mine showing the anhydrite complex. See Figure 2.

are controlled by the intersection of vein structures with contacts between marble, silicated, or hydrated alteration layers.

The ores show a mineralogical zoning with the Gertrudis stock roughly in the center. Enargite with tetrahedrite yields to chalcopyrite, tetrahedrite, and sphalerite away from the center. Toward the periphery of the district, sphalerite and galena are the dominant ore minerals. The zoning is also reflected in the increase of silver to copper ratio away from the center of the district. These are mesothermal deposits.

ANHYDRITE COMPLEX

The anhydrite complex is part of the limestone alteration which includes anhydrite and gypsum interbedded with layers of marble, silicated and hy-

drated "limestone," and shale. These alteration types are in layers and lenses of varying thickness with attitudes conformable to that of the western limb of the anticlinal structure (Fig. 3). The anhydrite is a soft but tough well knit rock that can remain open without support for several years. The rock is white to translucent with green and dark colored streaks of silicate minerals indicative of replaced bedding of the limestone. Layers in the anhydrite complex are commonly more highly contorted than the rather uniform attitude of bedding in the silicate alteration types and marble. The plastic behavior of this rock is reflected in the strong preferred shape orientation of the anhydrite grains (Figs. 4, 6, 7). In the upper part of the complex, the anhydrite is altered to gypsum.

Distribution.—Calcium sulfate was first noted on the 750 level, about 800 feet below the surface, near the Gertrudis stock. None has been found on or above the 400 level.

To the east, the anhydrite complex is bounded by a layer of hydrated "limestone" overlying the Catalina volcanics on the west limb of the major anticline (Fig. 3). The complex extends downward and westward and continues strong on the lowest level of mine development, the 1,700 level. Marble is most commonly interlayered with the anhydrite to the west, while to the east toward San Francisco stock, silicated and hydrated "limestones" are present to the exclusion of the marble.

Composition.—The gross composition of the anhydrite complex is that of discontinuous layers of anhydrite, marble, silicated and hydrated "limestone" alteration products, and shale. Shale layers are brown, generally less than 10 feet thick, and are replaced by anhydrite. The term "brown anhydrite" has been used locally and is more descriptive than shale.

Most anhydrite layers are 10 to 20 feet in thickness although some are as much as 100 feet thick. In the vicinity of Gertrudis stock, the apparent center of the complex, the layers are thickest. Contacts between various members of the complex are generally well delineated; hardness and color are generally sufficient for megascopic identification of the rock types. Distinction between the fine-grained anhydrite and gypsum, however, is more difficult. As revealed by thin section study, gypsum is the dominant calcium sulfate present from the 750 level to below the 1,000 level. Mine workings in this ground require more support than do those in the anhydrite below. The gypsum is dull white and consists of small fibrous grains, generally in random orientation. A preferred orientation of the gypsum is seen adjacent to replacement remnants of anhydrite grains (Fig. 5). Below the 1,000 level, anhydrite is dominant with gypsum in veinlets and replacing anhydrite grain borders (Fig. 4). Both gypsum and anhydrite are in small veinlets in all rock types surrounding the complex.

Other minerals in the anhydrite and gypsum layers are diopside, tremolite, calcite, talc, serpentine, quartz, zeolite, pyrite and magnetite. The silicates, except zeolite, are replacement residuals (Figs. 5, 8, 9). Calcite plays a dual role in that blocks of marble persist as replacement remnants, and also, late calcite veins the anhydrite. The late calcite veinlets are in turn cut by gypsum veinlets. Zeolite was noted only in the late gypsum veinlets. Pyrite,

associated with earlier silicate alteration of the limestone, is apparently unreplaced by the anhydrite. Many pyrite grains are rimmed with magnetite (Figs. 6, 7).

No ore bodies are found within the anhydrite itself but some of the district's richest copper ores are at the contact of the Gertrudis stock and the anhydrite. The anhydrite is coarsely crystalline and in places assumes a pinkish hue in contact with ore bodies. There is no apparent chemical reaction between the sulfides and sulfates, but recrystallization, possibly solution

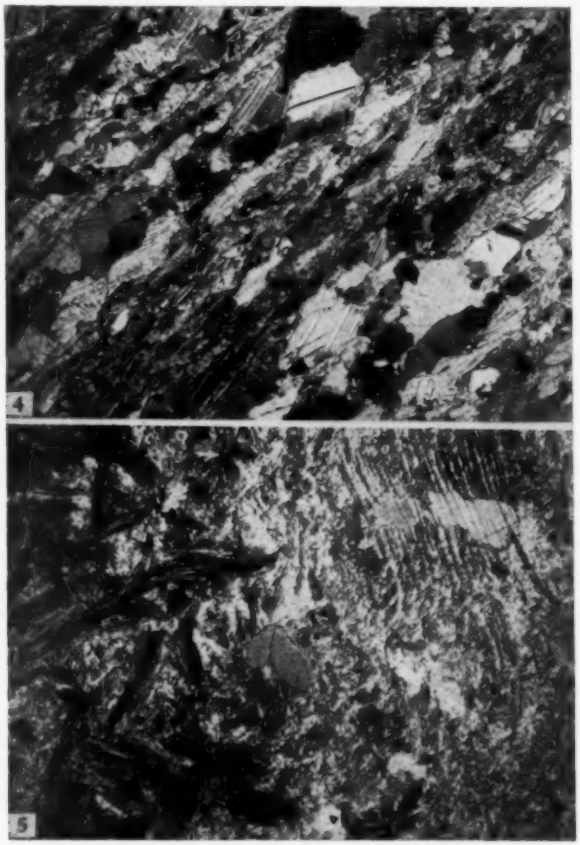


FIG. 4. Preferred shape orientation of anhydrite grains parallel to fine-grained gypsum replacement. Pyrite grains coated with magnetite. ×-nicols, × 18, 1,200 level.

FIG. 5. Fine-grained gypsum replacing tremolite on the left and anhydrite on the right. Twinning of anhydrite persists as relict structure in the gypsum. ×-nicols, × 18. 750 level.

and redeposition, has taken place. The thickness of this zone of recrystallization and discoloration is not more than 5 feet, and is therefore of little use as an ore indicator. Large crystals of selenite, up to a foot in length, are found only contiguous to or within ore bodies associated with the anhydrite.

THEORIES OF ORIGIN

Three possibilities of origin of the anhydrite at Morococha are: sedimentary, supergene, and hypogene. Haapala (9) suggested the possibility that the anhydrite is syngenetic with the Potosi formation. In support of this,

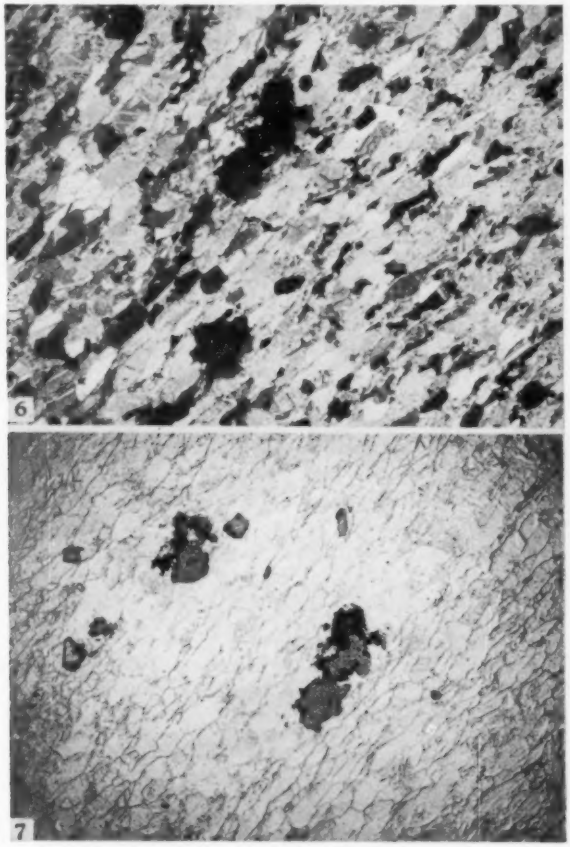


FIG. 6. Laminar structure by anhydrite grains. Black is pyrite coated with magnetite. ×-nicols, × 18. 1,200 level.

FIG. 7. The same section as Figure 6. Pyrite grains shown rimmed with magnetite. Plain light and reflected light, × 18.

Haapala cites the occurrence of a small evaporite gypsum deposit at Sacracancha, a few kilometers east of Morococha. If this deposit is in the Potosi limestone as indicated by Haapala, then it is possible that anhydrite or gypsum was also deposited in the Potosi formation to the west in Morococha. However, the small deposit at Sacracancha is either in the upper part of the Potosi formation or even in the Cretaceous Santo Toribio formation in contrast to the low position of the anhydrite in the Morococha Jurassic section. This small lens of gypsum is similar to many found in the Cretaceous sandstones and Tertiary red beds of Peru. The anhydrite at Morococha is intercalated with Jurassic limestones and is not typical of any Peruvian evaporite deposits.

The bedding in the anhydrite is more highly contorted than the bedding in the Potosi formation. This is offered by Haapala (9) as evidence that the anhydrite is at least as old as the folding of the sediments. However, anhydrite is a plastic rock, and even if subjected to stress only during the waning stages of tectonic activity, it might well be expected to show greater deformation than the more competent enclosing rocks.

Haapala's contention that anhydrite does not show the same spatial relationship to intrusives and known channelways as do the hydrated and silicated alteration types (9, p. 30) is quite correct, but this does not prove a syngenetic origin and, it will support the view that the anhydritization is of hypogene origin. In addition, the nature of the contact of anhydrite with the Gertrudis stock indicates that the anhydrite was later than the intrusion. There is no evidence of recrystallization, or even a slight coarsening in grain size of the anhydrite in contact with the stock, as would be expected had the stock intruded anhydrite.

The supergene theory or downward percolation and precipitation from meteoric waters may be eliminated inasmuch as it is improbable that anhydrite rather than gypsum would precipitate from cool waters under conditions of elevated pressure (1). Furthermore, a source above the Potosi limestone must be presumed, but there is no trace of calcium sulfate replacement between the 750 level and the surface.

The hypogene theory of origin is best suited to fit the sequence of alteration events interpreted from megascopic and microscopic examination of the anhydrite complex. The sequence is outlined as follows:

1. Intrusion of San Francisco stock with attendant formation of anhydrous and hydrous silicates in the Potosi formation.
2. Intrusion of Gertrudis stock followed by anhydritization of the Potosi formation.
3. Ore deposition.
4. Supergene deposition of calcite, gypsum, and zeolite.

The anhydrite complex is west of San Francisco stock and its associated silicate limestone alteration types. This suggests that the later Gertrudis stock intruded relatively unaltered limestone. The reasons for placing anhydritization after intrusion of Gertrudis stock and before ore deposition are as follows: (1). The grain size of the anhydrite is coarser near ore bodies as-

sociated with the stock, but shows no change in contact with the barren portions of the stock. (2). Spatial relationships indicate the stock to be the center of anhydritization. (3). Replacement textures dominate. All rock types in contact with the anhydrite, except ore bodies, show signs of replacement by anhydrite. Marble is almost completely replaced. The silicate alteration minerals are somewhat more resistant, but these too are mere remnants of former well developed crystals (Figs. 8, 9). Even the feldspars near contacts in the Gertrudis stock show attack by anhydrite.

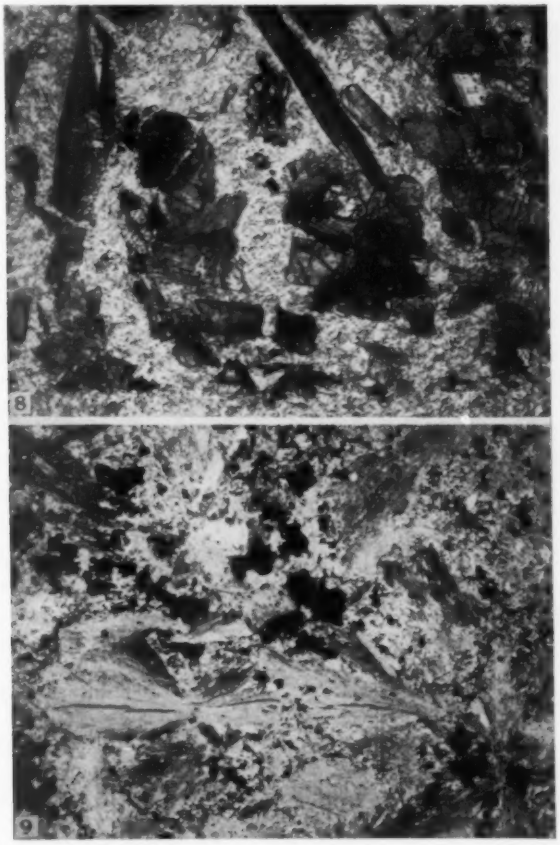


FIG. 8. Tremolite and diopside partially replaced by fine fibrous gypsum. ×-nicols, × 18. 750 level.

FIG. 9. Fine grained anhydrite replacing sheaf-like fibers of tremolite. Black grains are pyrite. ×-nicols, × 18. 1,700 level.

The problem of the hypogene theory lies in the conversion of limestone to anhydrite. This calls for solutions rich in the sulfate ion which were capable of replacing and removing carbonate ion, perhaps in the form of carbonic acid. It is interesting to speculate that the great mass of hydrated silicate alteration present above the complex was, in part at least, effected by this acid. Toward the San Francisco stock, the earlier silicate alteration of the limestone inhibited replacement by sulfate. To the west, near the Gertrudis reverse fault and surrounding the Gertrudis stock, the sulfate-bearing solutions found unaltered limestone available for replacement.

The question arises, why should alteration surrounding the Gertrudis stock be rich in sulfate while that surrounding the earlier San Francisco stock be rich in silicate? The answer must lie in a change in the alteration solutions associated with the intrusives. Certainly the oxidizing potential of the solutions was increased as indicated by the partial replacement of early pyrite by magnetite in the anhydrite complex (Figs. 6, 7). Such a condition is to be expected in the presence of heated solutions rich in the sulfate ion. Later, calcite, gypsum, and zeolite were deposited in the complex from downward percolating meteoric waters.

ORIGIN OF THE COLLAPSE BRECCIAS

The collapse breccias are associated only with the anhydrite complex. Commonly they are at intrusive contacts and in many places are associated with ore bodies. They are most prevalent in an elongate north-south zone on and above the 1,000 level at the eastern contact of the complex with the Catalina volcanics and the hydrated "limestone." The breccia fragments are mostly small, ranging from one-sixteenth inch to about six inches in size. They are generally sharply angular, supporting the idea that they are the product of collapse, and not tectonic activity. No slickensides, polished and striated sulfide minerals, or gouge are present in contrast to the abundance of these features in the tectonic breccias.

Depending upon the spatial relationships of the contacts, the breccias may be monomict or composed of several rock types. Since the breccias are above the 1,000 level, gypsum is the dominant calcium sulfate present. Solution of the gypsum is indicated by pits and hollows in the breccia fragments; less soluble silicate minerals project above the surface of the fragments.

The breccia zones have a limited vertical extent that rarely exceeds 300 feet. This is compatible with the theory of collapse and suggests that when the rate of collapse was greater than the rate of solution, the breccias eventually reached the back of the cavern and supported it.

Detailed mapping of anhydrite in contact with the quartz monzonite shows that below the 1,000 level the contact is firm; the anhydrite shows no sign of solution or recrystallization. Recrystallization of the anhydrite in contact with ore bodies is apparent, but no brecciation or even weakening of the anhydrite has occurred. This suggests that the solution of calcium sulfate, resulting in collapse and brecciation, has been accomplished by action of meteoric waters down to and slightly below the 1,000 level. This is more compatible

with the distribution of the breccias and the temperature-solubility relations of calcium sulfate. Gypsum in the ore bodies and in the upper part of the anhydrite complex indicates that it precipitated from cool solutions, less than 42° C (Posnjak, 1939). Furthermore, the solubility of calcium sulfate is greater in cool than in hot solutions. That meteoric waters have acted in the formation of solution caverns in anhydrite at Morococha is to be seen on the 1,000 level. Here, according to Moore (1936, p. 36), a cave measuring about 70 feet wide, 70 feet deep, and 130 feet long, was partially filled with water. Small stalactites of calcium sulfate were found on the walls of the cave.

These post-ore meteoric waters found easier descent along contacts than through the tightly knit mass of anhydrite. Although it is true that ore fragments do occur in part of these breccias, this is not the result of replacement of smaller particles of the breccia matrix with sulfides as claimed by Mark, Faulkner, and Graton (13, p. 240). The ore does not occur as a matrix of the breccia, and it is difficult to understand why only the smaller breccia fragments should be replaced whereas the larger fragments are quite fresh. The ores were deposited first and solution with slumping and brecciation followed.

CONCLUSIONS

The anhydritization at Morococha is a feature of limestone alteration by sulfate-rich solutions following the intrusion of the Gertrudis quartz monzonite stock. Ore solutions that followed anhydritization ascended along intrusive contacts with the anhydrite complex, and with the exception of minor recrystallization, wrought no great effect on the anhydrite. Descending meteoric waters converted the upper portion of the complex to gypsum, some of which was taken into solution. The resulting caverns slumped forming collapse breccias.

School of Mineral Sciences,
Stanford University,
Stanford, California.
March 22, 1957

REFERENCES

1. Bowles, O., and Farnsworth, M., 1925, Physical chemistry of the calcium sulphates and gypsum reserves: Econ. Geol., v. 20, p. 738–745.
2. Bowditch, S. I., 1950, Discussion of alteration and its application to ore search. Continuation of discussion: Colorado School of Mines Quart., v. 45, no. 1B, p. 280.
3. Boyle, A. C., 1914, The geology and ore deposits of the Bully Hill mining district, California: Am. Inst. Min. Met. Eng. Trans., v. 48, p. 67–115.
4. Butler, B. S., 1914, Geology and ore deposits of the San Francisco and adjacent districts, Utah: Econ. Geol., v. 9, p. 413–414.
5. Butler, B. S., 1919, Primary (Hypogene) sulfate minerals in ore deposits: Econ. Geol., v. 14, p. 581–609.
6. Butler, B. S., 1956, Mineralizing solutions that carry and deposit iron and sulfur: Mining Eng., v. 8, no. 10, p. 1012–1017.
7. Collins, J. J., 1950, Summary of Kinoshita's Kuroko deposits of Japan: Econ. Geol., v. 45, p. 363–376.
8. Haapala, P. S., 1949, On Morococha breccias: Bol. Soc. Geol. del Peru, Volumen Jubilar, Parte II, Fasc. 2, p. 1–11.
9. Haapala, P. S., 1953, Morococha anhydrite: Bol. Soc. Geol. del Peru, Tomo 26, p. 21–32.

10. James, H. T., 1929, Brittania Beach map-area, British Columbia: Canada Geol. Survey, Mem. 158.
11. Lacy, W. C., 1953, Differentiation of igneous rocks and its relation to ore deposition in central Peru: Bol. Soc. Geol. del Peru, Tomo 26, p. 121–134.
12. Langford, G. B., and Hancox, E. G., 1936, Hypogene anhydrite from the McIntyre mine Porcupine district, Ontario: Econ. Geol., v. 31, p. 600–609.
13. Mark, W. D., Faulkner, R. L., and Graton, L. C., 1942, Localization of certain ore bodies at Morococha, Peru: in Newhouse, W. H., Ore deposits as related to structural features, p. 238–241, Princeton, N. J.
14. Moore, T. G., 1936, The geology and ore deposits of Morococha, Peru: Unpublished doctoral dissertation, Harvard University, Cambridge, Mass.
15. Posnjak, E., 1939, The system $CaSO_4$-H_2O: Amer. Jour. Sci., v. 35a, Series 5, p. 247–272.
16. Sales, R., 1950, Discussion of alteration and its application to ore search, Continuation of discussion: Colorado School of Mines Quart., v. 45, no. IB, p. 284.
17. Schmedeman, O. C., 1940, Recent studies of the geology of the Morococha district, Peru: Proc. Eighth Amer. Sci. Congress, v. 4, p. 677.
18. Terrones, A. J., 1949, La estratigraphia del distrito minero de Morococha: Soc. Geol. del Peru, Vol. Jubilar, XXV Aniversario, pte. II, fase 8, p. 1–15.

THE OCCURRENCE OF ZINC IN SOIL

M. L. WHITE

ABSTRACT

This paper describes procedures for determining the form in which zinc is held in soil. The procedures involve removal of the iron oxide and determination of the associated zinc, a similar treatment of the clay size material to determine, indirectly, the lattice-held zinc, and an ammonium chloride extraction to determine the base-exchanged zinc. Values for the distribution of zinc in some Tennessee soil composites are given.

ALTHOUGH a good deal of work has been done on studying the availability or extraction of zinc from soils with different reagents, very little has been done on determining, experimentally, how the zinc is held in the soil. Hibbard (1) found that the zinc content of soils decreased as the particle size increased and that a small amount of zinc normally in soil is not exchanged with ammonium or calcium ions, which suggested that some of the zinc was in the clay mineral structure. Jones (2) showed that when zinc sulfate was added to a soil three classes of compounds were formed: (1) water soluble; (2) those with replaceable zinc; and (3) water insoluble and non-replaceable compounds. He found that as the added zinc concentration was increased more of the zinc occurred as the insoluble form. Thorne (3) found some correlations in Utah soils between zinc content and pH, zinc content and organic matter, and total and available zinc. Elgabaly (4, 5) treated clay minerals with zinc solutions and found that with montmorillonite, less than 70 per cent of the added zinc could be leached out with NaCl, $CaCl_2$ or HCl solutions, suggesting fixation of some zinc in the clay mineral lattice. Recently, Nelson and Melsted (6) studied the chemical form of zinc added to the soil, using Zn^{65} in an isotope-dilution technique. They found that in an H^+-soil system practically all the added zinc was replaceable by an ammonium acetate solution, while in a Ca^{++}-soil part of the zinc was not replaceable, the amount of this zinc increasing with increasing length of time of contact between the soil and the zinc solution.

This type of work has suggested some possible zinc associations, but a survey of the literature shows that only limited efforts have been made to determine experimentally how zinc is held in the soil. The purpose of this paper is to present some work that was done to determine quantitatively in what forms zinc occurs in soils.

EXPERIMENTAL METHODS AND MATERIALS

The analysis for zinc was carried out by a titrimetric dithizone method modified after the procedure described by Sandell (7). Fifty or 100 mg of air dried -80 mesh soil, or the residue from the bleaching treatment described later, is fused with 1 g of potassium pyrosulfate. The fused residue is ex-

tracted with hot water and the extract titrated with 0.0016 per cent (w/v) dithizone in carbon tetrachloride in the presence of approximately 0.2 N ammonium citrate solution, buffered at pH 8.2. The titration is carried out by adding measured increments of the dithizone solution, shaking, settling and discharging the reacted dithizone until an increment remains green on shaking. The total volume of dithizone solution used is compared with the amount required to titrate a known zinc solution and the metal content reported as ppm. zinc. This method detects copper, lead and zinc as an undifferentiated group reported as zinc equivalent. Previous work has shown that in the soils studied, 80 to 100 percent of the mineralization (total zinc, lead and copper) was zinc, so that for the purposes of this work the ppm values are considered as zinc only.

Iron oxide was removed from the soils by a method modified after that described by Aguilera (8). In this method the soil is treated with a hot solution of sodium hydrosulfite, sodium citrate and versene, so that the iron in the form of the oxide is reduced by the hydrosulfite and removed by complexing with the citrate and versene. The bleached residue of soil resulting from this treatment has been changed from the original only in that any iron oxides have been removed. Aguilera found that iron in such forms as ilmenite or silicates is not attacked, and the structure of clay minerals is not affected, so that iron (or zinc) in the lattice position of such minerals would not be removed. The latter conclusion was checked and confirmed by the author. It was found, however, that when zinc was adsorbed from solution on clay minerals, this exchangeable zinc was removed by the above treatment.

The clay-size fractions of the soils were separated by centrifuging a 5-percent aqueous suspension of the soil, dispersed with sodium tripolyphosphate, in a 200-ml glass jar at a speed and for a length of time calculated from Stokes Law (9) in order to separate the < 2-micron size. Two settlings were made on each sample, as previous work had shown that this removed more than 90 percent of the clay-size material.

The usual method of determining base-exchanged ions consists of an extraction of the soil with 1 N NH_4Ac (pH 7.0) using a number of successive extractions. From experiments on clay minerals with added exchangeable zinc it was found that a single extraction with 5 N NH_4Cl adjusted to pH 8.0 with NH_4OH removed about 80 percent of the exchangeable zinc, which for the purposes of this work was considered sufficient. The extraction was carried out by allowing 0.5 g of -80 mesh soil to stand in contact with 20 ml of the NH_4Cl solution for 15 minutes with occasional shaking. The suspension is then centrifuged, the clear supernatant solution decanted and analyzed for zinc with 0.00064 percent (w/v) dithizone (in carbon tetrachloride) using a photometer for measuring the color change, and determining the amount from a calibration curve.

The samples used for this study were taken in the Copper Ridge area in Hancock, Hawkins and Grainger Counties, Tennessee. The soils here are predominantly cherty silt loams in the Clarksville and Fullerton Series, overlying dolomitic limestone. All samples were taken with a slotted tube at a depth of two feet, which would generally place them in the B horizon. For

the present study, from 20 to 30 samples were chosen randomly in areas of about six acres (square plots 500 feet on a side). All the samples within such an area were mixed together, after being air-dried, and the composite ground to pass an 82-mesh cloth sieve. Fourteen such areas were studied.

ASSOCIATION OF ZINC WITH IRON OXIDE

From both field and laboratory observations it is apparent that there is a definite and direct relationship between the zinc content and iron content of many soils, this conclusion being supported by the following facts: (1) In many locations it is found that the concentration of zinc in limonites is always higher than in the surrounding soil; (2) in many areas there is a definite correlation between the percent iron and the percent zinc in subsurface soils; and (3) when

TABLE 1

ASSOCIATION OF ZINC WITH IRON OXIDE IN SOILS

Composite Number	Total ppm Zn in Soil	Ppm Zn in Bleached Residue	Ppm Zn Associated with Iron Oxide and Base-exchanged	% of Total Zn Associated with Iron Oxide and Base-exchanged
1	151	78	73	48
2	132	78	54	41
3	316	126	190	60
4	143	62	81	57
5	357	188	169	47
6	146	85	61	42
7	259	138	121	47
8	127	75	52	41
9	271	137	134	49
10	123	87	36	29
11	809	434	375	46
12	141	77	64	45
13	1,015	579	436	43
14	159	106	53	33
				Average 45

some soils are separated into size fractions, there is a correlation between the zinc and iron contents of the various sizes, i.e., the size fraction having the highest zinc content also has the highest iron content, and vice versa.[1]

Since most of the iron in the soils studied in the Eastern United States is in the form of hydrous ferric oxides it would appear that a good deal of the zinc must be tied up with this iron oxide. If this is so then removal of the iron oxide from a soil should also remove some zinc. In order to test this idea the soils were treated to remove the iron oxide and the amount of zinc removed was also determined.

When iron oxide is removed from soils by the treatment previously described and the bleached residue analyzed for zinc, it is found that some of the original zinc in the soil has been removed along with the iron oxide. This extracted zinc is likely the sum of that in base-exchangeable form and that

[1] Unpublished work of the author.

associated with the hydrated iron oxide in some type of solid solution or adsorption compound. It will be shown later that in general, less than 3 percent of the total original zinc is base-exchanged, so that although the mineralization extracted by the bleaching treatment includes both that associated with the iron oxide and that which is base-exchanged, the latter generally represents a minor part of the total extracted. By subtracting the ppm zinc in the bleached residue from that in the original soil it is possible to calculate the percent of total mineralization associated with (or removed with) the iron oxide.

Table 1 shows the results of the bleaching treatment on the 14 composite samples. The last column gives the percent of the total original zinc which is associated with the iron oxide plus that which is base-exchanged in the soil.

TABLE 2

ZINC HELD IN LATTICE OF CLAY MINERALS IN SOILS

Composite Number	Total ppm Zn in Soil	Ppm Zn in Bleached Residue of Clay-size	Wt. % Clay Size	% of Total Zn in Clay Mineral Lattice
1	151	241	13	21
2	132	202	15	23
3	316	366	29	34
4	143	160	28	31
5	357	436	35	43
6	146	196	27	36
7	259	345	33	44
8	127	193	30	46
9	271	347	29	37
10	123	217	26	46
11	809	1,248	21	32
12	141	200	25	35
13	1,015	1,457	25	36
14	159	258	18	29
				Average 35

These figures vary from 29 percent to 60 percent with an overall average of 45 percent. This indicates that about half of the total zinc in the soils is associated with the hydrous iron oxides. The exact nature of this association is not known, but may be in the form of a simple absorption type compound or a solid solution of zinc in iron oxide. Such an association of zinc with iron oxide is not surprising in view of the highly adsorptive property of ferric oxide for other metal ions forming insoluble hydrous oxides (10).

LATTICE-HELD ZINC

Some important constituents of soil with regard to zinc associations are the clay minerals, which are generally found only in the clay-size fraction (< 2 microns). It is known that zinc can replace aluminum in the lattice structure of montmorillonite, forming the mineral sauconite (11). It can be assumed that all the zinc in the clay-size fraction of a soil which is not as-

sociated with the iron oxide or base-exchanged is contained in the lattice sites of the clay minerals, since in general the clay-size fraction of a soil contains only three types of materials: (a) clay minerals; (b) iron oxide, either amorphous or as crystalline geothite or hematite; and (c) quartz or possibly amorphous silica (12). It seems reasonable to expect the zinc content of quartz or silica to be negligibly small.

The clay-size fractions of the soils were separated, the total zinc content of the material was determined, and then a portion of it treated to remove iron oxide. The zinc content of the bleached clay residue is due primarily to the lattice held zinc, so that by multiplying the ppm. zinc in the bleached residue of clay times the weight percent of the clay-size material, and dividing by the total original ppm zinc in the soil, the percent of total mineralization held in

TABLE 3

EXCHANGEABLE ZINC IN SOILS

Composite Number	Total ppm Zn in Soil	Ppm Zn Extracted by 5 N NH_4Cl, pH 8.0	% of Total Zn Extracted by 5 N NH_4Cl, pH 8.0
1	151	3.9	2.6
2	132	2.2	1.7
3	316	6.0	1.9
4	143	2.4	1.7
5	357	10.6	3.0
6	146	10.2	7.0
7	259	3.2	1.2
8	127	2.0	1.6
9	271	4.2	1.5
10	123	0.9	0.7
11	809	11.5	1.4
12	141	9.3	6.6
13	1,015	10.6	1.0
14	159	7.3	4.6
			Average 2.6

the lattice of the clay minerals is obtained. Table 2 shows these values for the 14 soil composites. It is seen that the amount of zinc presumed held in the lattice position of the clay minerals varies from 21 percent to 46 percent of the total zinc in the soil, with an overall average of 35 percent.

BASE-EXCHANGED ZINC

There is considerable evidence in the literature that natural soils contain exchangeable zinc. Hibbard (1) found that small amounts of zinc are removed from soils by leaching with solutions of sodium acetate, ammonium acetate, potassium chloride and other reagents which are known to remove base-exchanged ions. This was confirmed by Thorne (3) who found that a 0.05 N KCl solution acidified to pH 3.2 extracted measurable amounts of zinc from the soil.

Table 3 shows the values for the amounts of zinc removed by the NH_4Cl extraction of the 14 soil composites. The per cent of total mineralization ex-

tracted varies from about 1 percent to 7 percent with an overall average of 2.6 percent. These values are similar to those found by Hibbard (1) and Baughman (13) and indicate the relatively small amount of zinc which is held in exchangeable positions.

SUMMARY OF LOCATION OF ZINC IN SOIL

Table 4 summarizes the data for the location of the zinc in the 14 soil composites studied. The figure for the per cent of total zinc held by the iron oxides has been corrected for the base-exchanged zinc in this table by subtracting the percentage values in Table 3 from those in Table 1.

TABLE 4

DISTRIBUTION OF ZINC IN SOILS

Composite Number	Total ppm Zn in Soil	% of Total Zn in			Total %
		Iron Oxide	Clay Lattice	Exchange Position	
1	151	45	21	3	69
2	132	39	23	2	64
3	316	58	34	2	94
4	143	55	31	2	88
5	357	44	43	3	90
6	146	35	36	7	78
7	259	46	44	1	91
8	127	39	46	2	87
9	271	47	37	2	86
10	123	28	46	1	75
11	809	45	32	1	78
12	141	38	35	7	80
13	1,015	42	36	1	79
14	159	28	29	5	62

From the figures in the last column it can be seen that from 60 percent to 90 percent of the total zinc has been accounted for, leaving 10 per cent to 40 percent that occurs in some form, other than those shown. There are other possible ways in which zinc might be held in the soil:

(1) With organic matter: It has been shown by Baughman (13) that up to 66 percent of the total zinc in a soil can be held by organic matter in a soil that contains about 9 percent of the latter. However, since the soils studied for this work were all taken at a two-foot depth, the amount of organic matter is probably quite small, so that only a relatively small percentage of the total zinc would be held in this manner.

(2) In resistant minerals: Such minerals as magnetite, ilmenite, zircon, etc., occur to some extent in soils and it is not unlikely that they could contain a considerable amount of zinc that would not be removed by any of the above procedures, except in the total zinc analysis. It has been found, for example, that ilmenite separated from a soil in Saucon Valley, Pa., contained 1,000 ppm zinc.

Although the percent of total zinc unaccounted for is as high as 40 percent the corresponding absolute zinc values are generally less than 50 ppm, so that

a small amount of organic matter or resistant mineral with a relatively high zinc content could account for the remaining portion of the zinc.

SUMMARY

When the iron oxide is removed from a soil by a reduction-complexing series of reactions, about half of the total zinc in the soil is also removed. This portion of the mineralization is concluded to be associated with the iron oxide.

That part of the mineralization in the clay fraction of the soil that is not associated with the iron oxide is considered to be held in the lattice portion of the clay minerals. Finally, the amount of base-exchanged mineralization is determined separately by extracting the soil with an ammonium chloride solution.

When the percentages of total zinc held in each of these ways is determined on a number of composite soils from Tennessee, it is found that from 30 to 60 percent of the total zinc is held with the iron oxide, from 20 to 45 percent is held in the lattice position of the clay minerals, and from 1 to 7 percent is base-exchanged in the clay minerals. When the individual percentages are totaled for each composite, the sum varies from 60 to 90 percent, that is from 10 to 40 percent of the total zinc has not been accounted for, depending on the particular sample under consideration. It is proposed that this unaccounted zinc, which in most cases amounts to less than 50 ppm, can be traced to zinc held with organic matter or in resistant minerals.

RESEARCH DEPARTMENT,
NEW JERSEY ZINC CO.,
PALMERTON, PA.
March 11, 1957

REFERENCES

1. Hibbard, P. L., 1940, The chemical status of zinc in the soil with methods of analysis: Hilgardia, v. 13, p. 1–29.
2. Jones, H. W., et al., 1936, The reaction of zinc sulfate with the soil: Florida Agr. Exp. Sta. Bull. no. 298, p. 5–43.
3. Thorne, D. W., et al., 1942, Zinc relationships of some Utah soils: Soil Sci., v. 54, p. 463–468.
4. Elgabaly, M. M., and Jenny, H., 1943, Cation and anion interchange with zinc montmorillonite clays: Jour. Phys. Chem., v. 47, p. 399–408.
5. Elgabaly, M. M., 1950, Mechanism of zinc fixation by colloidal clays and related minerals: Soil Sci., v. 69, p. 167–173.
6. Nelson, J. L., and Melsted, S. W., 1955, The chemistry of zinc added to soils and clays: Soil Sci. Soc. Am. Proc., v. 19, p. 439–443.
7. Sandell, E. B., 1944, Colorimetric determination of traces of metals: Interscience Publishers.
8. Aguilera, N. H., and Jackson, M. L., 1953, Iron oxide removal from soils and clays: Soil Sci. Soc. Am. Proc., v. 17, p. 359–364.
9. Prutton, C. F., and Maron, S. H., 1949, Fundamental principles of physical chemistry: Macmillan Co., New York.
10. Weiser, H. B., 1935, Inorganic Colloid Chemistry: John Wiley & Sons, New York.
11. Ross, C. S., 1946, Sauconite—A clay mineral of the montmorillonite group: Am. Mineralogist, v. 31, p. 411–424.
12. Robinson, F. W., 1951, Soils: John Wiley & Sons, New York.
13. Baughman, N. M., 1956, The effect of organic matter on the retention of zinc by the soil: Ph.D. Thesis, Purdue University.

HEAVY METAL CONCENTRATION IN STREAMS IN NORTH ANGOLA

D. J. ATKINSON

ABSTRACT

In order to determine the extent and characteristics of temporal variation in the heavy metal content of surface streams in north Angola, a series of observations was made in the vicinity of known mineralization in the Bembe valley during five months of 1955. It was found that during the dry season concentrations were stable but low. They became very high and variable in the early rains: later in the rainy season they fell irregularly to very low, but stable, values.

INTRODUCTION

GEOCHEMICAL methods of prospecting have now become established as aids in the search for orebodies, which may be indicated by anomalous secondary dispersions of heavy metals in soils, vegetation, stream sediments, and natural waters.

Few data have so far been published on heavy metals in natural waters, but advance in this field of geochemistry has been more rapid since 1948, when details were published of a colorimetric method of measuring very small amounts of heavy metals (the "dithizone" field test—Huff, 1948). Prior to the development of this test by the United States Geological Survey several studies of trace elements had been made, using various methods of analysis. Vogt and Rosenqvist (11), working in Norway, concluded that high copper concentrations in streams of the Røros district were related to hidden orebodies, and Sergeev (6) working in the Altai Mountains in Russia reached a similar conclusion in areas of polymetallic mineralization. Huff (2) in addition to describing the dithizone field test gave details of anomalous concentrations (in Gilpin County, Colorado), which were traced upstream to mine drainage. While pointing out that ore deposits opened up by mine workings inevitably suffer accelerated weathering and may be expected to discharge large quantities of heavy metals into the drainage system, he remained hopeful that unknown, hidden orebodies might yet be traced by analyses of natural waters. Working on the San Manuel copper deposit in Arizona, Lovering, Huff and Almond (3) considered that very little copper was dissolving in the ground water, and that prospecting by this method was not likely to be successful under such conditions. Chisholm (1) found that it was possible to detect zinc mineralized shear zones on the shores of a lake in Ontario by tests made on water within five feet of the shore. In the Nigerian lead-zinc belt, Webb and Millman (10) found marked increases in heavy metal content where streams crossed lodes, but noted considerable differences between values re-

corded when the same points were tested on three different occasions. These variations, they suggested, were perhaps an expression of the balance between dilution by run-off, and increases in metal supply as a result of increased ground-water movement. Riddell (4), in the Gaspé Peninsula, Quebec, noted variable amounts of heavy metals in the streams; he was able to correlate some high concentrations with known base metal occurrences, but in other cases the cause of high values was not discovered. The same writer later carried out more detailed work in a small area within the peninsula; comparison of the results of soil analyses and water analyses showed that though anomalous concentrations in streams corresponded well in many places with high values in soils, the results of water analyses were somewhat erratic, and gave negative indications in some areas of known mineralization where soils yielded strong positive anomalies.

Modifications of the "classical" dithizone test designed to give greater sensitivity have been described by Warren, Delavault and Irish (8, 9) who pointed out that in the Pacific Northwest, as a result of heavy run off from rain, melting snow, and icefields, prospecting by water analysis is only feasible with a test capable of detecting 0.001 ppm of heavy metal.

The present work was intended, first, to discover whether a known but little disturbed copper deposit in Angola gave rise to anomalous metal concentrations in the surface streams, and if its position could be traced from the pattern of heavy metal values in the drainage system, and secondly, to study the seasonal and daily variations in values at selected points in order to find the best method of carrying out hydrochemical prospecting in this region, and the best season for such work.

This study, which was carried out while the writer held the position of geologist with Empresa do Cobre de Angola, had to be combined with other duties, and as a result it was not always possible to keep continuous records. The results are thus somewhat incomplete, but are considered sufficiently interesting to be recorded.

LOCAL CONDITIONS

The experiments were carried out in the Bembe valley, 160 miles north-east of Luanda and 230 miles south-west of Leopoldville. The ore body is situated along a reverse fault crossing the country in a north-westerly direction and dipping steeply to the south-west. On the north-east side of the fault are a series of slates and sandstones; to the south are limestones, overlain by sandstones in such a way that the outcrop of the latter reaches the fault at the western, higher end of the valley. Mineralization is in the form of irregular nodules and bodies, and also veinlets and stringers of malachite; other oxidized copper minerals are present in subordinate amount, with some black hydrated oxides of manganese.

The deposit has been worked sporadically since before 1855 but work ceased in 1945 due to the high cost of extracting the ore. Mining operations have been mainly confined to the shaded area shown on Figure 1; apart from two prospect shafts in the positions indicated, only a few trenches and trial cuts have disturbed the surface.

The Bembe river runs close and sub-parallel to the fault, which outcrops on the scarp of the north side of the valley and is crossed by a series of tributaries feeding the main Bembe river.

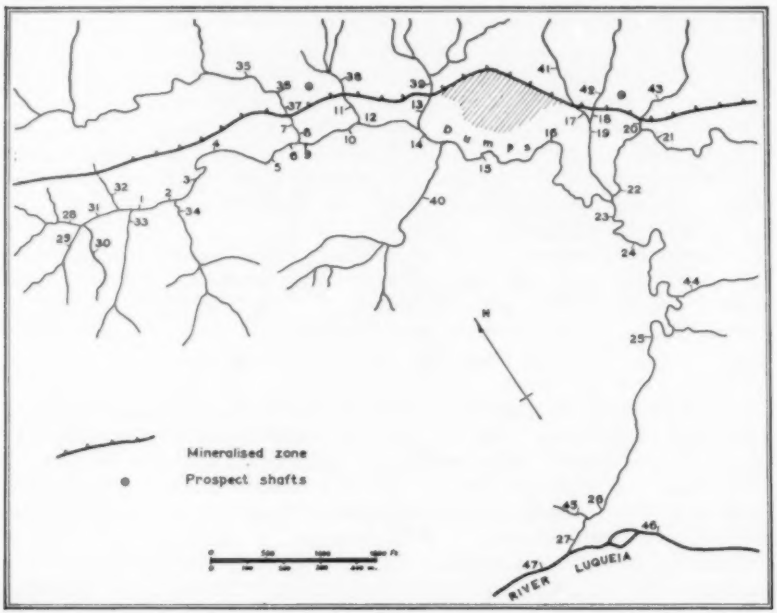


FIG. 1. Sites of water tests in the Bembe valley.

The yearly cycle of weather changes at Bembe is as follows: there is a period of four months without any rain from mid-May to mid-September; the rainy season that follows is divided into two parts by a short dry period of about a month in January to February. The rainy season is preceded by an "intermediate period" of about four weeks during which slight precipitation

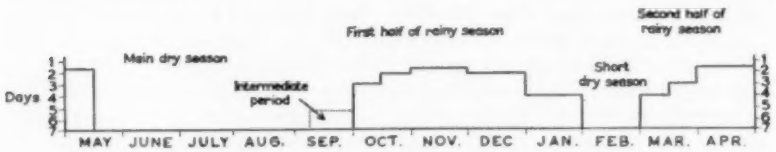

First half of rainy season
Second half of rainy season
Main dry season
Intermediate period
Short dry season
Days
MAY JUNE JULY AUG. SEP. OCT. NOV. DEC JAN. FEB. MAR. APR.

FIG. 2. Average interval between successive rains.

(lasting up to an hour or two) sometimes occurs from heavy early morning mist, known in Angola as "cacimbo." The frequency of rain in each month is shown in Figure 2. During the first half of the rainy season, November is generally the wettest month; during the latter half, April and early May

are characterized by rain almost every day. The temperature in the dry season is generally fairly low, mostly below 70° F; in the rainy period it is hotter, somewhere in the range 85° F to 100° F at mid-day.

TECHNIQUE

The experiments were carried out with the "McPhar Water Testing Kit" —a very light and readily portable field apparatus specially designed so that no cleaning is involved in its use. A complete description of the apparatus and its use has been given by Wark (7). The procedure is briefly as follows: 50 ml of the water sample is placed in a small graduated Pyrex bottle; the pH is adjusted to between 8.5 and 9 by the addition of 1 ml of a buffer-complexer-indicator solution. Successive additions of 1 ml of dithizone are made, and shaken for 30 seconds, until the droplets collected at the bottom of the bottle change in color from red to a standard shade of purple. While the droplets are red, an excess of metal dithizonates is indicated; when the purple shade is reached there is an excess of dithizone and the reaction is complete, the flask thus being automatically cleaned after each test. The quantity of dithizone used gives the concentration in the sample; each 1 ml addition (to a 50 ml water sample) reacts with 0.01 ppm of heavy metal.[1] When less than 0.01 ppm of heavy metal is present, the droplets formed when the first 1 ml of dithizone is added have a color in the range green-blue-grey-dark purple-purple, corresponding to increasing concentrations between zero and 0.01 ppm. It is thus possible to detect and roughly distinguish between these very small values. The additions of buffer solution and dithizone are made from small polyethylene dispensing bottles, and measured in a small flask set on the inside of the graduated test bottle itself. Risk of contamination is thus reduced to a minimum.

The dithizone was dissolved in reagent grade chloroform. A stock 0.1 percent solution was diluted daily to give a 0.001 percent solution for the tests.

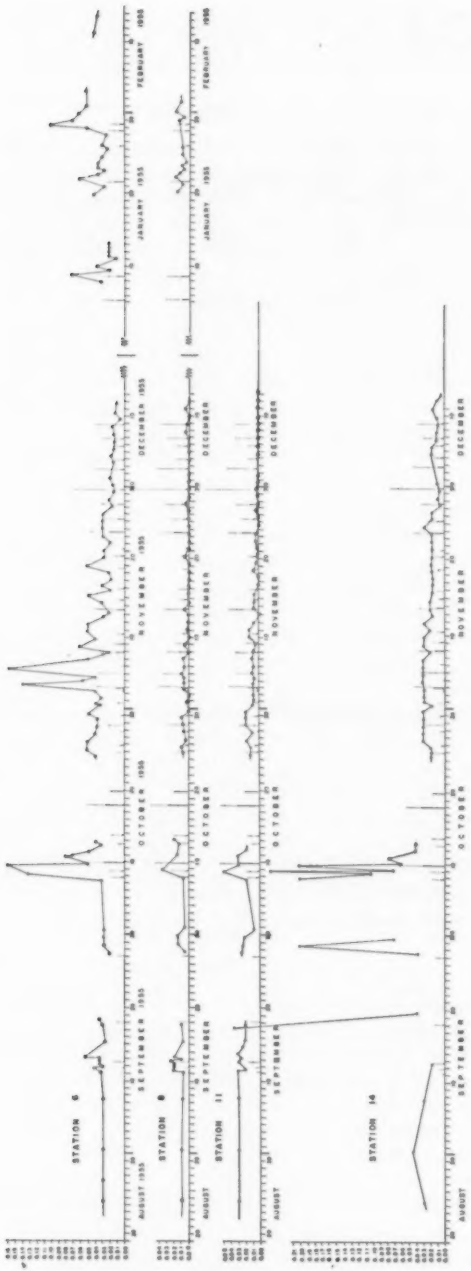
Water samples were in some cases tested on the spot, but most were stored between one and four days until about thirty or forty specimens had accumulated, and could be dealt with together. This reduced the time involved in testing and also the amount of chloroform used. The samples were stored and collected in 400 ml glass-stoppered Pyrex bottles, which were rinsed three times in the stream water before being filled to the brim. Check tests on stored samples showed that no deterioration occurred.

RESULTS

Preliminary tests in January and February 1955 showed that the heavy metal concentration in streams in areas of barren rocks was far less than 0.01 ppm. Where streams crossed the mineralized zone this concentration increased noticeably (to as much as 0.10 ppm) and water sampling traverses proved capable of tracing the line of mineralization. However, observations at selected points showed considerable day-to-day variation in the values of heavy metal concentration.

[1] All metal concentrations in this paper are expressed as zinc equivalents.

TEMPORAL VARIATION OF HEAVY METAL CONCENTRATIONS



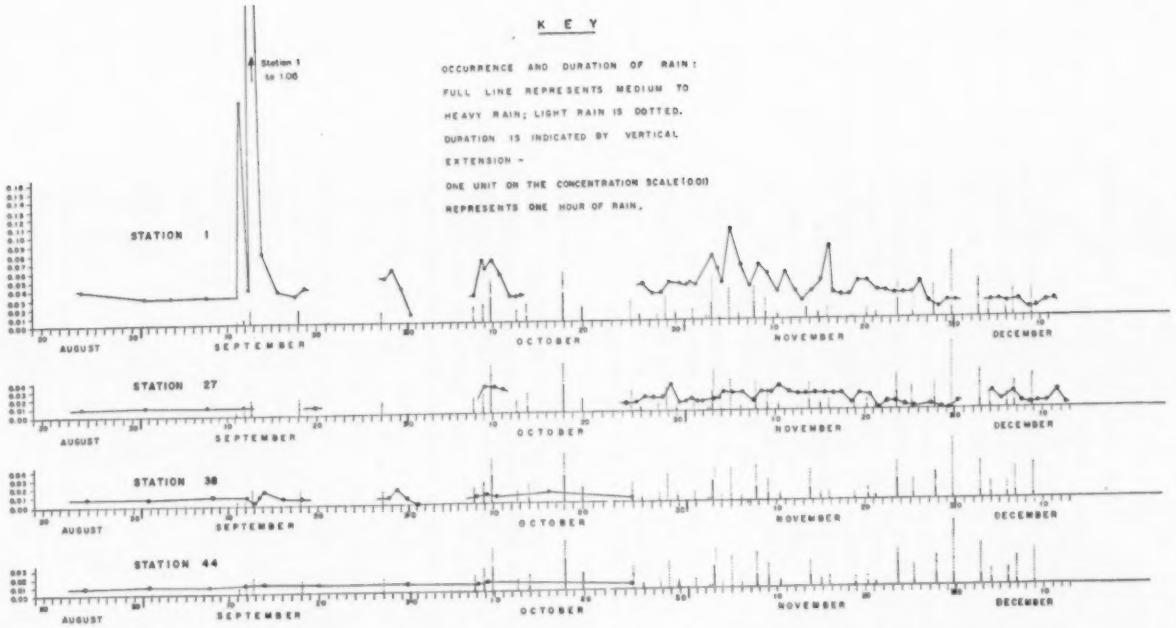


FIG. 3. Daily observation of rainfall and metal concentrations at eight points in the Bembe river system.

In order to study the variation in detail, daily observations at eight points were made as continuously as possible over the period August to December, which represented the latter part of the dry season, and the whole of the first part of the rains. These observations were accompanied by a detailed record of rainfall, water levels, and other relevant features. The sites of the stations are shown in Figure 1, and the results of the tests are plotted graphically in Figure 3. Each rain is represented by a vertical line.

The first three plots refer to stations a short distance downstream from the mineralized zone. Station 6 is about 90 m from the fault plane: Station 8 is about 50 m, and Station 11 about 60 m from it.

The three plots show similar features: steady, moderately low readings in the dry season were followed by small temporary increases after each of a series of five heavy "cacimbos" in the intermediate period between September 12th and October 7th. These involved very slight precipitation from early morning mist, lasting between 15 minutes and 1½ hours.

On October 8th, 10 days after the last of these heavy "cacimbos" the values at all three stations had returned to the level recorded during the dry season. On the evening of October 8th, there occurred one hour of heavy rain, followed by showers for a further 40 minutes. Readings the following morning —12 to 14 hours after the rain—showed three- to five-fold increases in the metal concentration, Station 6 giving a value of 0.13 ppm.

As the graph for Station 6 shows, there was, during the succeeding period from October 8th to early December, a close link between rainfall and the heavy metal concentration. Rain generally occurred in the evenings, and observations twelve hours later almost invariably showed a marked increase relative to the value recorded before the rain. Very high values again occurred after two prolonged rains, on November 3rd and 5th. After that there was a steady decline in the peak values following rains, until by December a reading in excess of 0.02 ppm was never attained. Stations 8 and 11 exhibited similar features except that no very high values occurred after those of the first true rains (October 8th–10th). Although the results obtained at these two Stations do not show such a clear correlation between increased values and rainfall, particularly in the last month of observations, a general decrease in peak values is again apparent until, after five or six weeks of rains, "zero" readings (< 0.002 ppm) were frequently given by the test.

It seems reasonable to assume that the broad features of the seasonal variation in metal concentration are the same from year to year, and accordingly the plots of values at Stations 6 and 8 for January and February 1955 have been placed in such a way as to succeed those of December. It appears that the low values of the latter part of the first rainy period (October–December) are followed by another period of extreme variability in the short dry season, when heavy rains are separated by dry intervals of 7 to 14 days or more. Thus, readings at Station 8 again rise to 0.02 ppm, whereas values for Station 6 reach 0.10 ppm and show a particularly clear relation to the incidence of rainfall. It is expected that had it been possible to continue observations over the second part of the rainy season (February–May) the plots of values

would have shown a similar (but probably more rapid) decline to very low values, as occurred in the first part of the rains.

Station 14 was situated below the main area of old workings and some dumps, and received water that had passed through this zone of accelerated weathering and oxidation. From October 8th onwards the values show a pattern of change very similar to those described above. During the dry season, however, there is variability and in the period of "cacimbos" preceding the rains proper, extreme instability is observed: readings of as much as 0.36 ppm were recorded; observations were too sporadic to establish a relation between mist precipitation and increased values, if it existed. The very high and variable readings of the intermediate period and the moderately high and somewhat variable values of the dry season, seem likely to be the consequence of the position of this station with respect to the old workings and dumps.

Station 1, situated in an area of undisturbed mineralization, showed similar extreme variability in the metal content of the water, particularly during the first four days of precipitation from mist, when a value of 1.06 ppm was recorded (September 13th): the concentration rapidly fell, however, to below 0.08 ppm. After the first short period of very variable, very high values, it is again seen that rainfall was frequently followed by an increase in heavy metal concentration. The extended rains of October 3rd to 5th were followed by high readings (0.07, 0.10 ppm), as at Station 6. Again readings showed a tendency to decrease until, in December, a value of 0.02 ppm was never exceeded (cf. August to November, when a value as low as 0.02 ppm was only recorded twice).

This Station lay within an area of disseminated sulfides in the sandstones on the south side of the fault (about 100 m from the fault plane). Here, during the dry season, the sandstones at the surface showed a coating of leached and oxidized material. The first light rain rapidly washed out this very soluble accumulation and this was undoubtedly the cause of the extremely high local concentrations (up to 1.06 ppm) observed during the first period of light precipitation.

Station 27 was located in the River Bembe just above the point where it enters the much larger river Luqueia. The metal content of the Luqueia above the confluence is too small to measure accurately using the McPhar kit, but was estimated as being generally less than 0.001 ppm. The addition of the metal-charged Bembe waters to the Luqueia river is not sufficient to raise the concentration to 0.01 ppm, but a definite increase is detectable from the "stronger" color (i.e., more purple, less blue) produced by the addition of the first 1 ml of dithizone solution; the content is, however, estimated as less than 0.005 ppm.

The object of locating Station 27 in this position was to discover whether a series of tests at tributary mouths on main rivers would lead a prospector using the McPhar kit to a deposit of the Bembe type. From experience in the country around Bembe, values of 0.02 ppm and less were regarded as of no significance; values exceeding this figure seemed to warrant further investigation. Marked dilution of high values close to the main fault takes place very rapidly as one passes downstream and, for most of the year, con-

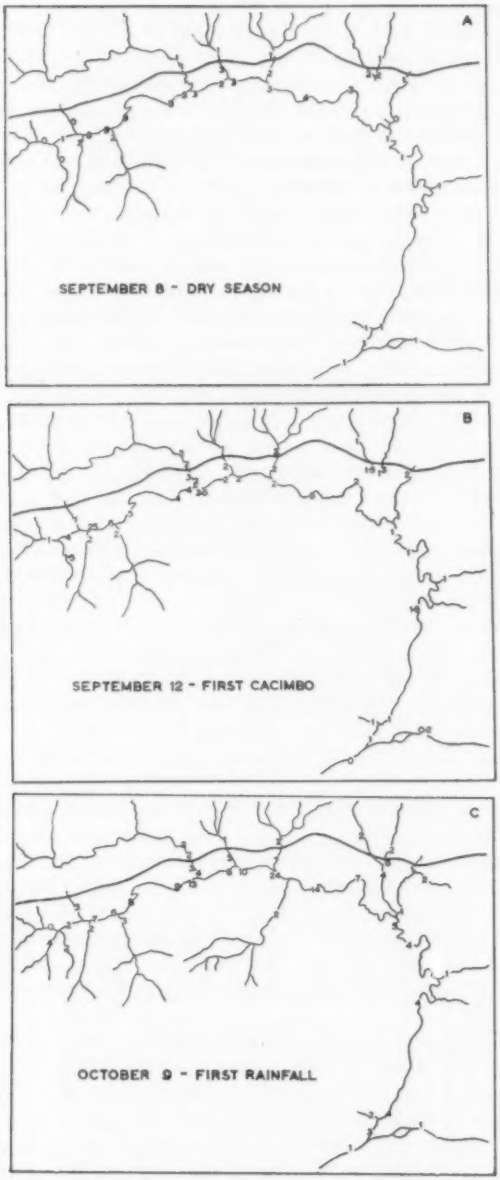


FIG. 4. Heavy metal concentration patterns. (Concentration as parts per *hundred* million.)

centrations exceeding the significant level—0.02 ppm—do not persist as far as Station 27. However, as Figure 3 shows, significant values were recorded after the first true rains (Oct. 8th–11th) and on two subsequent occasions (Oct. 30th and Nov. 11th). Readings in the dry season were very low (0.01 ppm or less). In the rainy season they were moderately high at first, but

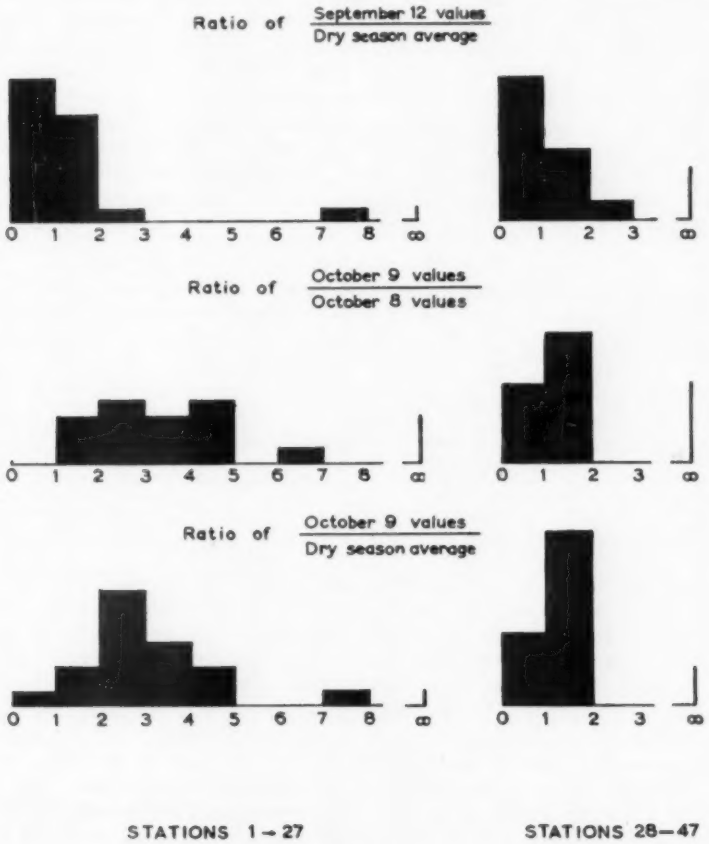

Ratio of September 12 values / Dry season average
0 1 2 3 4 5 6 7 8 ∞
0 1 2 3 ∞
Ratio of October 9 values / October 8 values
0 1 2 3 4 5 6 7 8 ∞
0 1 2 3 ∞
Ratio of October 9 values / Dry season average
0 1 2 3 4 5 6 7 8 ∞
0 1 2 3 ∞
STATIONS 1 – 27
STATIONS 28–47

FIG. 5.

there followed a progressive, though very slight decrease. Even in December, however, when most of the stations close to the source of the metal were giving readings appreciably less than their dry season level, values at Station 27 still frequently rose above 0.01 ppm (the constant reading of the dry season). This is a result of local differences in the relative distribution of run-off in the dry and rainy seasons.

TABLE 1

Station	A Dry season —av.	B Sept. 12	B – A	B/A	C Oct. 8	D Oct. 9	D – C	D/C	D – A	D/A	Station
1	3.3	25	+21.7	x7.5	3	7	+4	x2.3	+3.7	x2.1	1
2	3	6	+3	x2	3	6	+3	x2	+3	x2	2
3	3.5	5	+1.5	x1.4	3	8	+5	x2.7	+4.5	x2.3	3
5	3.3	4	+0.7	x1.2	—	9	—	—	+5.7	x2.7	5
6	3	4	+1	x1.3	3	13	+10	x4.3	+10	x4.3	6
7	1	3	+2	x3	0	3	+3	x ∞	+2	x3	7
8	1	2	+1	x2	1	4	+3	x4	+3	x4	8
9	2.3	3.5	+1.2	x1.6	2	4	+2	x2	+0.7	x1.7	9
10	2.3	2	−0.3	x0.9	2	6	+4	x3	+3.7	x2.6	10
11	2.6	2	−0.6	x0.7	2	5	+3	x2.5	+2.4	x1.9	11
12	2	2	0	x1	2	10	+8	x5	+8	x5	12
13	2.2	2	−0.2	x0.9	1	7	+6	x7	+4.8	x3.2	13
14	3	2	−1	x0.6	20	24	+4	x1.2	+21	x8	14
15	4	5	+1	x1.2	3	14	+11	x4.7	+10	x3.5	15
16	3.3	2	−1.3	x0.6	2	7.5	+5.5	x3.7	+4.2	x2.3	16
17	1.3	1.3	0	x1	1	—	—	—	—	—	17
18	2	3	+1	x1.5	—	6	—	—	+4	x3	18
20	1.5	2	+0.5	x1.3	0	1	+1	x ∞	+0.5	x0.7	20
22	0	1	+1	x ∞	0	1	+1	x ∞	+1	x ∞	22
23	1	1	0	x1	1	5	+4	x5	+4	x5	23
24	1	1	0	x1	1	4	+3	x4	+3	x4	24
25	1.5	1.5	0	x1	—	4	—	—	+2.5	x2.7	25
26	1	1	0	x1	—	4	—	—	+3	x4	26
27	1	1	0	x1	—	3	—	—	+2	x3	27
28	0	1	+1	x ∞	0	0	0	x1	0	x1	28
30	0	1.5	+1.5	x ∞	0	2	+2	x ∞	+2	x ∞	30
31	1.5	4	+2.5	x2.7	1	2	+1	x2	+0.5	x1.3	31
32	0	1	+1	x ∞	—	3	—	—	+3	x ∞	32
33	1.5	2	+0.5	x1.3	—	2	—	—	+0.5	x1.3	33
34	2	2	0	x1	2	3	+1	x1.5	+1	x1.5	34
36	1	2	+1	x2	0	2	+2	x ∞	+1	x2	36
37	1	2	+1	x2	1	2	+1	x2	+1	x2	37
38	1	1	0	x1	1	1	0	x1	0	x1	38
39	1	2	+1	x2	1	2	+1	x2	+1	x2	39
41	1	1	0	x1	1	2	+1	x2	+1	x2	41
42	1	1	0	x1	0	2	+2	x ∞	+1	x2	42
44	1	1	0	x1	1	1	0	x1	0	x1	44
45	1	1	0	x1	—	2	—	—	+1	x2	45
46	1	0.2	−0.8	x0.2	—	1	—	—	0	x1	46
47	1	0	−1	x0	—	1	—	—	0	x1	47

Concentrations in *parts per hundred million*.

The lower two graphs of figure 3 indicate conditions at Stations 38 and 44, points in the country rock area where the water is unaffected by the Bembe mineralization. Station 44 gave steady readings of 0.01 ppm throughout the period of great variability discussed above and also after the first true rains. Station 38 showed some small variation (in the range 0 to 0.02 ppm) during the early heavy dewfalls, but in the dry season and through the first heavy rains the concentration remained steady at 0.01 ppm.

The observations discussed above are confirmed by detailed records at two other stations, Numbers 12 and 15. In addition, observations on the concentration pattern over the whole river system were made on various occasions.

The metal content at all stations was measured three times during the latter part of the dry season (between late August and mid-September). Average values are given in Table 1, column 1. In general, readings were extremely consistent; only in the case of Stations 14 and 15 did any observations differ from the average by as much as 0.01 ppm. Values on September 12th after the first precipitation (15 minutes of very light drizzle) are given in column 2; and in columns 3 and 4 the relations (difference and ratio) between dry season readings and those of September 12th are shown. The table also includes values recorded before and after the first true rain of October 8th and gives the relation between these values. Figure 4 illustrates these observations; in addition histograms have been constructed to show the distribution of ratio values more clearly (Fig. 5). In these diagrams the stations have been divided into two groups, namely, those liable to be affected by the known mineralized zone (Stations 1 to 27), and those which lie outside its influence (Stations 28 to 47).

TABLE 2

RATIOS OF CONCENTRATIONS AT STATIONS BELOW AND ABOVE MINERALIZED ZONE

Stations	Dry season	After first cacimbo	Before first rain	After first rain
$\frac{8}{37}$	1	1	1	2
$\frac{11}{38}$	2.6	2	2	5
$\frac{13}{39}$	2.2	1	1	3.5

The histograms for the ratio between September 12th values and those of the dry season, are similar for the two groups. About half the stations fall in the 0–1 block, that is to say the readings of September 12th showed no increase, or a reduction, relative to dry season values. The other stations show increases up to 3 times, except Station 1, discussed above, which gave an increase to 7.5 times. In the histograms for the ratio between readings on October 9th and October 8th it is seen that only 20 percent of the "barren" stations showed an increase of more than 2 times. In the case of streams draining mineralized ground, however, 75 percent give a ratio greater than 2. The third pair of histograms, comparing dry season values with those of October 9th, have essentially the same appearance as those relating October 8th and October 9th, confirming that the increases did not occur generally until after the first rains.

The conclusions that may be drawn are that although local high concentrations may occur during the "intermediate period," it is not until the true rains begin that values show a marked increase over those of the dry season. Then, as is seen in Table 1, there is an increase in all values, which is much more marked in those streams crossing the mineralized zone. The period of the early rains is thus one of increased sensitivity, when the contrast between

values upstream and downstream of a metal source, is exaggerated. The numbers in Figures 6 and Table 2 are taken from three streams crossing the mineralized zone; the ratio between the heavy metal concentration below and above the zone is shown for each river on four occasions: during the dry season; after the first light drizzle from "cacimbo;" and before and after the first rain.

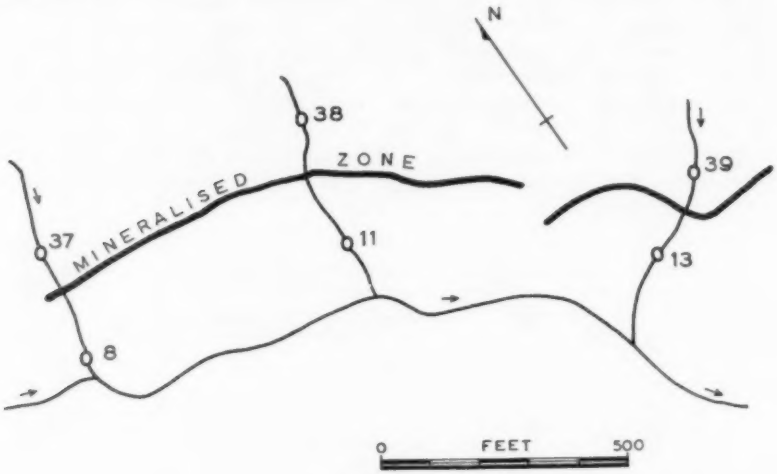


FIG. 6.

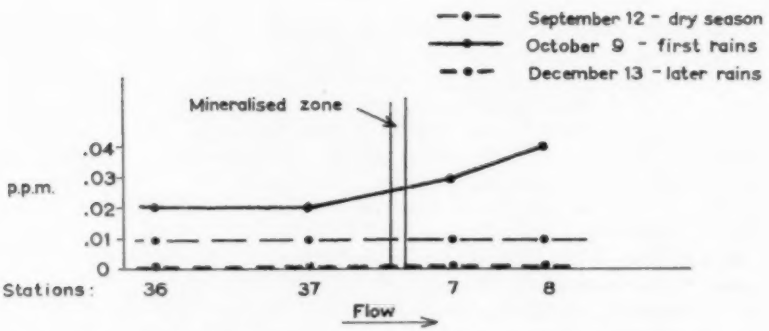


FIG. 7. Hydrochemical traverses along one tributary crossing the mineralized zone.

A series of detailed traverses along one stream flowing across the mineralized zone further illustrates this point. The tests were made at three different times during the year and the results (Fig. 7) show that the zone is only detectable in the early rains, not in the dry season, nor during the later rains.

The early period of exaggerated contrast (at the beginning of the rainy season), which probably lasts only a week or two, is however also one of considerable variability, so that comparison of figures obtained in a regional survey and not measured simultaneously, would be very difficult. Later in the rainy season the day-to-day variation is much smaller but there is then less contrast, all readings being low (in general lower than in the dry season). At this time, comparison of values from one area to another is much easier as a result of the reduced amount of daily variation, but the loss of contrast be-

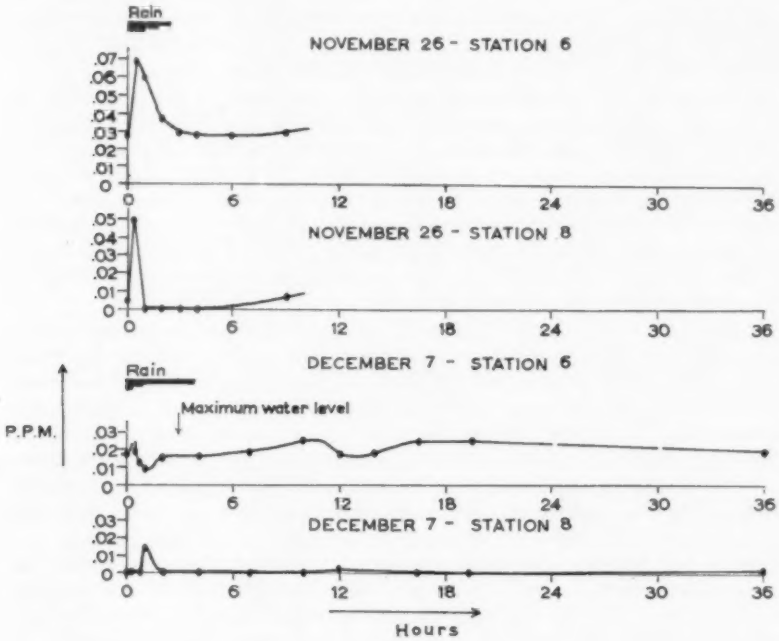


FIG. 8.

tween anomalies and background may then make detection of sources of heavy metal extremely difficult. It is possible that a more sensitive test may overcome this difficulty.

The short dry period is seen from the observations of January–February 1955 to be another period of increased contrast and increased variability. Values in the second half of the rainy season will almost certainly show a similar decrease in contrast and variability as in the first half.

In order to investigate the mechanism involved in the variations in heavy metal concentrations, a detailed hour-by-hour study was made of the changes in the period following a fall of rain. The results are shown in Figure 8.

The rainfall on 26th November was preceded by a dry period of two days, while that of 7th December was after a dry interval of only one day.

Time did not allow the writer to follow up this aspect of the work, but it was already plain that metal concentrations in the streams reflect the balance between two factors: dilution by surface run-off on one hand, and the amount of metal entering the surface drainage on the other. The metal comes mainly from ground water although some is derived from sources at or near the surface, as at Station 1 where disseminated mineralization outcrops, and Station 14 where similar conditions have been created artificially by dumping. In general, these surface sources have only minor effects, except during a very short period at the end of the dry season when the soluble leached products, accumulated over a period of months, are washed out suddenly.

The transfer of metal through ground water, from the ore body into the surface drainage, is more constant; but it may be postulated that when the water table falls during dry spells, it leaves behind a zone in which metal is precipitated, to be flushed out by the next rain. The extent of this zone will depend on the length of the dry interval, i.e., the height through which the water table falls; and the amount of metal carried into the surface drainage by the rain that ends a dry interval will be, in part, proportional to the length of the interval. But in addition, the heaviness of the downpour will determine how much of the total metal content of the zone is flushed out.

Towards the end of the dry season, the zone will attain its greatest extent, the water table being very low. It appears that the light drizzle from "cacimbo" during the intermediate period is not heavy enough to flush out more than a very small amount of material: this process only begins when the true rains start. Then the increase in metal supply is so great that, despite the large volume of surface run-off, concentrations rise to very high values.

The constancy and lowness of the concentrations recorded in December seems to be the result of the very short interval between successive rains and to correspond to a period in which the water table is high and oscillates frequently, but through only small distances. Earlier in November, when the interval between heavy rains is longer, the water table is lower and has time to fall through greater distances during the relatively dry periods; in these conditions there may be some precipitation and accumulation of metals between rains. But the very high values of November 3rd and 5th, after the two prolonged rains, suggest that at that time there still remained a good deal of material accumulated during the dry season and not yet washed out.

These suggestions concerning the processes involved in temporal variation in metal concentration are put forward very tentatively. Insufficient work has been done on this aspect of the subject to justify definite conclusions. The chief result of the work has been to determine the characteristics of variation in metal content of the surface waters, and to link this with season and rainfall.

ACKNOWLEDGMENTS

My thanks are due to the Directors of Empresa do Cobre de Angola for their permission to publish the results of this study; to Dr. J. S. Webb for

his helpful criticism of the manuscript; and to Mr. Pedro Alberto for his help in the collection of water samples.

MANIWAKI, QUEBEC,
March 12, 1957

REFERENCES

1. Chisholm, E. O., 1950, A simple chemical method of tracing mineralisation through light non-residual overburden: Canadian Inst. Min. Metallurgy Trans., vol. 53, p. 44–48.
2. Huff, L. C., 1948, A sensitive field test for heavy metals in water: ECON. GEOL., vol. 43, no. 8, p. 675–684.
3. Lovering, T. S., Huff, L. C., and Almond, H., 1950: Dispersion of copper from the San Manuel copper deposit, Pinal County, Arizona: ECON. GEOL., vol. 45, no. 6, p. 493–514.
4. Riddell, J. E., 1952, Preliminary report on hydrochemical analyses of streams and rivers in the Gaspé peninsula: Prov. Quebec, Dept. Mines P. R. No. 268.
5. Riddell, J. E., 1954, Geochemical soil and water surveys in Lemieux Township, Gaspé-North County: Prov. Quebec, Dept. Mines P. R. No. 302.
6. Sergeev, E. A., 1946, Razvedka Nedr., vol. 12, no. 2, p. 51–55. Translated by H. E. Hawkes: Water analysis as a means of prospecting for metallic ore deposits. Precambrian, vol. 26, no. 6, p. 18–19, 41, 1953.
7. Wark, W. J., 1955, Geochemical prospecting in lakes and rivers: Canadian Min. Met. Bull., vol. 48, no. 516, p. 195–198.
8. Warren, H. V., Delavault, R. E., and Irish, R., 1951: Improved dithizone field test for heavy metals in water: Geol. Soc. America Bull. 62, p. 609–618.
9. Warren, H. V., Delavault, R. E., and Irish, R., 1953, Acetonic dithizone in geochemistry: ECON. GEOL., vol. 48, no. 4, p. 306–311.
10. Webb, J. S., and Millman, A. P., 1950, Heavy metals in natural waters as a guide to ore. A preliminary investigation in West Africa: Inst. Min. Metallurgy Trans., vol. 59, p. 323–349.
11. Vogt, T., and Rosenqvist, A., 1942, Determination of copper in natural waters from the Røros District: Kgl. Norske Videnskabs. Selskab. Forh., Bd. 15, no. 23, p. 87–90.

ON THE OCCURRENCE OF URANIUM IN ANCIENT CONGLOMERATES

CHARLES F. DAVIDSON

ABSTRACT

In recent discussions on the origin of the mineralization of the Witwatersrand and of Blind River, various departures from actualistic principles have been postulated by geologists of the placerist school in necessary support of their views. None of these hypotheses stands up to critical examination; and from consideration of the mineralogy and geochemistry of the banket reefs it is concluded that the mineralization is certainly not of alluvial origin. Claims that detrital uraninite can be recognized in mineragraphic studies lack due objectivity. Because of reworking of the uranium and the probable presence of old radiogenic lead, it is not yet possible to place any reliance on the apparent ages recorded for these banket ores. In speculation on the source of the pay-metals, it is suggested that the mineralization may be linked to periods of granitization late in the history of the Witwatersrand and Huronian geosynclines.

INTRODUCTION

THE greatest deposits of uranium ore discovered during the world-wide explorations of the last decade are the conglomerate reefs or "bankets" of the Witwatersrand and of Blind River. Together these two mining fields will, by the end of this year, supply around three fifths of the western world's uranium to the value of more than £100 million annually. The South African and Canadian provinces are sufficiently similar in their structural geology and geochemical characteristics to suggest strongly that the mineralization, however it was effected, must be attributed to the same causes in each case. In each field the principal ore bodies are reefs of quartz-conglomerate of wide lateral extent, bearing uraninite, gold and sulfides, and interbedded with arkoses and other quartzose sediments in which mineralization, if present at all, is very much less pronounced. In any one conglomerate reef of the Witwatersrand there tends to be a sympathetic relationship between the tenor of uraninite, of gold, and of pyrite; but the relative proportions of these minerals may vary greatly from one reef to another within the same province. In South Africa it is exceptional to find a uranium content high enough for the radioactive metal to be recovered commercially save as a by-product of the gold. In Canada, on the other hand, the conglomerates are payable for uranium alone and the "patchy" gold is no more than a problematical by-product of the future. In a third comparable province, the Serra de Jacobina of Bahia, Brazil, the same association of uraninite, gold, and pyrite in conglomerate reefs occurs (69), but here it has not yet been demonstrated that

the rocks are adequately mineralized to warrant large-scale mining for any of the contained minerals.

The association of uraninite, gold, and pyrite common to these three fields suggests that the three minerals have a community of origin, that they form a trinity which, regarded from the aspect of ore genesis, must be considered as an indivisible whole. The South African mines have been sampled for gold and uranium more fully and systematically than any other group of deposits in the world, and it is now generally accepted that the sympathetic relationship between the tenor of gold and content of uranium indicates beyond all doubt that the two metals are co-genetic. Sampling for pyrite and other sulfides has been nothing like so extensive, but a great many workers in South Africa, Canada, and Brazil have remarked on the general parallelism in content of sulfides, uranium and gold. It would seem that for deposits of this kind consanguinity of pyrite, uranium and gold is as irrefutable as is a common parentage of the metals commonly found together in polymetallic fissure veins.

The origin of this type of ore deposit has been the topic of a long-continued controversy, centered principally upon the Witwatersrand; and despite intensive study it has not been possible to bridge the gap between two schools of thought. One of these attributes an alluvial origin to the pay metals, believed to be deposited with the conglomerate as placer gold, detrital uraninite and sedimentary pyrite (or iron ores which later became sulfidized), followed by subsequent metamorphism under "pseudo-hydrothermal" conditions that obliterated most evidence of sedimentary genesis. The other regards the mineralization as epigenetic, introduced into the conglomerates by fluids either emanating from subjacent igneous intrusions or otherwise permeating throughout the sedimentary rocks late in the formational history of the geosynclines of which the strata form part. The sedimentary control of the mineralization is such that more than £3,500 million worth of gold has been produced in South Africa since the discovery of the field in 1886, as a result of mining development following certain conglomerate reefs; and since at first sight placer origin and sedimentary control seem synonymous, it is not surprising that the alluvial theory has become the more acceptable to many mining geologists. On the other hand, as the hydrothermal theory is better supported by geochemical evidence, does not demand the departure from the doctrine of uniformity which placerist views necessitate, and gives a better basis for primary exploration for new ore-fields, it has been the more favored by many geologists not concerned with day-to-day mining operations.

The present paper attempts a critical review of the contributions to this controversy published subsequent to the discovery of the important concentrations of uraninite in the bankets. These contributions comprise principally papers by the writer (15, 16, 19) favoring, on geochemical grounds, a hydrothermal origin for the ores, and monographs by Ramdohr (55) and Liebenberg (45) presenting mineragraphic studies in support of a placer derivation. The resolution of the differences between the two schools is one of the most important problems of economic geology to-day, for not until a better understanding of the origin of the ore-bodies is reached will it be possible to make a systematic scientific approach to the problems of discovering new ore fields.

THE GEOCHEMISTRY OF THE BANKETS

Until very recently, Government regulations have prohibited the publication of information on the grade and extent of uranium ore deposits, and reasoned argument on the genesis of mineralization has been inhibited by the lack of quoteable analytical data. To remedy this deficiency an indication of the grade of the mineralization present in the principal banket fields is given in the table below. These data, culled from sources of varying reliability, do not pretend to any great precision.

	U_3O_8, percent	ThO_2, percent	Gold, dwt./ton	Pyrite, percent	Thickness, feet
Witwatersrand reefs, South Africa	0.01	0.000x	5.5	2–10	3–4
Dominion reef, South Africa	0.09	0.00x	<1	?	3
Blind River reefs, Ontario	0.11	0.03	trace	5–25	10–14
Pyritoso reef, Brazil	0.01	?0.000x	<1–5	?5–25	2

From the geochemical aspect, the most interesting feature of this tabulation is a demonstration of the poverty of the bankets in thorium relative to uranium. In all normal sedimentary rocks (phosphorites, marine black shales, and some limestones excepted) the thorium content is much in excess of the tenor of uranium; and in highly weathered sediments such as sandstones and conglomerates the thorium:uranium ratio is commonly 10:1 or more (1). The inference is, therefore, that the bankets are not sedimentary assemblages.

In previous papers the writer (15, 16) has reviewed the available information on the radioactivity of modern placer deposits worked for gold. From first-hand studies of some thousands of samples collected from alluvial gold-fields in New Zealand, Gold Coast, Sierra Leone, Belgian Congo, Northern Rhodesia and Colombia, supplemented by published data on material from Canada, Alaska, California, Idaho, Mexico and the U.S.S.R., it has been possible to demonstrate conclusively (a) that in all instances where significant radioactivity is found in an alluvial gold-field, thorium is present in marked excess over uranium; (b) that the radioactivity of such auriferous sediments nowhere remotely approaches that of the banket reefs; and (c) that such radioactivity in modern alluvials is always attributable to refractory minerals (monazite, thorite, euxenite, samarskite, xenotime, malacon, etc.) which are rare in the bankets, and never to uraninite which is common in these pyritic conglomerates.

There are few empiricisms in geology to which an occasional exception may not be found; but notwithstanding the intensive world-wide explorations for uranium, no single observation antagonistic to the above conclusions has yet been reported. On the contrary, the supporting field evidence has recently grown considerably. Thus a study of the alluvial gold-fields of Angola (9), undertaken in search of uranium, has demonstrated that the heavy concentrates are characterized by "a large proportion of rare earths, thorite, columbo-tantalates and cassiterite"—but no uraninite. Along river courses in Southern Rhodesia (52) the radioactive minerals in the auriferous alluvium are

monazite and thorite; and in Mozambique (9) the heavy minerals of placer deposits investigated as a source of uranium are only "ilmenite, magnetite, garnet, zircon, monazite, samarskite and columbite." Further afield, in Korea (72) the gold-bearing placers are characterized by monazite, xenotime, fergusonite, samarskite, columbite and tantalite—never uraninite, though this is present rarely, together with gold, in Korean pegmatites. An identical association is seen in the placers of Japan (29). A very extensive study of the radioactive minerals present in gold and other placers in many parts of the United States, investigated in no less than 48 exploration projects of the U. S. Bureau of Mines, has revealed similar detrital assemblages with only one recorded "trace" of uraninite (24). In Idaho uraninite is present with gold in bedrock veins close to the placers exploited for their radioactive mineral content; but even in this environment it is absent from the alluvial assemblages.

If attention is not restricted to auriferous placers, but extended to sands and gravels of all kinds, the evidence that in such rocks thorium is always dominant over uranium and that these radioactive elements are present principally in refractory minerals becomes completely overwhelming. Of over 60,000 concentrates from almost every alluvial mining field throughout the free world examined in recent years by the writer and his former colleagues, only one showed a high content of uranium relative to that of thorium. This sole exception was a highly radioactive discard from tin-mining operations in the Phuket-Phangnga region of Thailand (14), in which monazite and euxenite (with some samarskite and brannerite) are present in roughly equal proportions, giving a thorium:uranium ratio of close to unity.

That there may be exceptional circumstances in which uraninite can *occur* as a detrital mineral is undeniable. Reference has been made many times in recent discussions to a concentrate reputedly taken by a prospector from a placer deposit in British Columbia (61), which is said to contain, as accessory minerals in decreasing order of abundance, monazite, scheelite, platinum, uraninite, cinnabar and gold; but despite the obvious economic interest of this "sample" it has not been possible to repeat it in four years of fevered prospecting. If genuine, it presumably derives from very close to bedrock mineralization—just as detrital torbernite may, in a desert terrain like that of Mount Painter in South Australia, occur in the immediate vicinity of a uranium lode. But the question is not whether uraninite occurs as a detrital mineral—it is whether it *persists*. Of this persistence no evidence has ever been found. On the contrary, the writer (19a) has shown that on a beach in Cornwall, which is fed by mine debris, uraninite introduced as pebbles does not survive as the coarser debris becomes comminuted to sand. Again, in a study of the gravels in modern streams draining those areas of the Colorado plateau that contain workable uraninite deposits, Chew (10) has shown that the radioactivity becomes undetectable by a sensitive scaler-type Geiger counter at distances of more than a mile down valley from the mines or mills.

A geochemical peculiarity of the Witwatersrand reefs not, so far as we know, shared by the other bankets is the presence of osmiridium. Cousins (11) has shown that in the Witwatersrand ores there is a sympathetic variation between the tenor of uranium and that of osmiridium; and arguing from

the assumption that the latter is "undoubtedly of placer origin" he concludes that the uraninite is likewise detrital. But the alluvial nature of the osmiridium is very far from certain. Most of the samples of this mineral hitherto studied have been from amalgam barrel residues, hence depleted of gold and bearing a pseudo-detrital form due to the shaping of malleable particles in the ball mills. The photomicrographs of Liebenberg (45), however, demonstrate that in the banket the iridosmine is intergrown with gold and thus must be co-genetic with the gold (of acid origin) rather than with the chromite (of basic origin). Now, this very association of gold, uranium and platinoids that we find in the Witwatersrand is one that is characteristic of several deposits throughout the world. It is well known in the uranium ores of Athabaska, where the precious metals vary sympathetically and exceptionally may be present in phenomenal amount (32); it is seen in the great uranium deposit of Shinkolobwe (21), where the sludges left on leaching the uraninite concentrate contain many ounces of gold per ton, with a significant tenor of palladium and platinum; and it is also evident in a small gold-uranium-platinoid deposit at Ruwe in the Belgian Congo, last worked in 1938 to yield that year some 1,800 oz. of platinoids from an ore containing around 4 dwt. of platinoids and 3 dwt. of gold per ton. While, therefore, Cousins assumes that the sympathetic relationship between gold, uranium and osmiridium furnishes proof of the placer origin of the uranium, there seem to be sounder grounds for viewing this same relationship as indicative of the epigenetic nature of the osmiridium.

In an earlier paper, the writer (16) has commented that "whilst the likely congeners of placer uraninite are absent from the [Witwatersrand] reefs, those minerals and metals which habitually accompany uranium of hydrothermal origin are invariably present." This remark is equally applicable to the Blind River field. Chalcopyrite, sphalerite, galena, stibnite, pyrrhotite, arsenopyrite, skutterudite, cubanite, linnaeite, cobaltite, niccolite, pentlandite and related species have all been recorded in mineragraphic studies of the bankets. The presence of a significant cobalt mineralization is only too well known to the metallurgist in South Africa. In the Rand the uranium is recovered from solution by means of anion exchange resins, following the removal of the gold by cyanidation; and the cobalticyanides formed in the cyanidation tailings form strong "poisons" inhibiting the most efficient use of the resins. At Blind River not only are cobalt and copper sulphides and arsenides present in small amounts in the reefs, but transgressive shear vein deposits in the same district, at Pater Uranium Mines, are mineralized with these metals to a workable extent. Since cobalt is the most common companion of uranium in undoubted hydrothermal associations, the co-existence of the two elements in the banket is another strong argument against a syngenetic origin.

The radiometric logging of bore holes throughout the Witwatersrand, undertaken principally by Simpson (58, 59, 60), has provided a fund of data of which the interpretation is still somewhat obscure; but one most remarkable feature of these logs that must be accommodated in any theory of ore genesis is that the radioactivity of the rocks in any major section of the sequence tends

to vary directly as the particle size in the sediments. In any single sedimentary cycle within the System the radioactivity progressively decreases as one passes from conglomerate through quartzite and argillaceous quartzite to shale. As Simpson himself has noted (59, p. 140), this is the reverse of the radioactivity distribution pattern to be seen in any sequence of normal strata. This abnormality suggests very strongly that the distribution pattern of the uranium is in no way attributable to sedimentary processes, except in so far as it is governed by the permeability of the strata.

These geochemical arguments are strong; and to counter them South African geologists have found it necessary to postulate that the "detrital" ores accumulated under various non-actualistic conditions which are discussed below.

SOME *DEI EX MACHINA*

The convincing accumulation of evidence that uraninite does not survive in modern alluvial deposits has recently led geologists of the placerist school to amend the views that they have long maintained on the sedimentary origin of the Witwatersrand ores. It is now held that although the bankets represent fossil alluvial deposits with placer gold and detrital uraninite, the deposits accumulated under conditions quite at variance with those of the present day, thus invalidating actualistic arguments based upon the doctrine of uniformity. The game is no longer played according to Lyell.

Thus Louw (47) has suggested that the gold and uraninite are both detrital, and that at the time of their deposition the Earth's atmosphere was a reducing rather than an oxidizing environment, thus supposedly favoring preservation of the uranium mineral. Weibols (70) propounds a theory that the major reef horizons of the Witwatersrand originated under glacial conditions, the uraninite notionally being protected from comminution and dissolution by enclosure in boulder clay. Bain (4) is of the opinion that the uraninite was refractory to decay since it was liberated as detrital grains at a time prior to the establishment of a land flora, when terrestrial waters supposedly were neither acid or alkaline. Liebenberg (45) gives good measure: boldly ignoring the incompatibility of his various premises, he favors an atmosphere of carbon dioxide with some free oxygen (but regards reducing conditions as "not unlikely"!) together with glacial conditions and with ground waters having a near neutral pH. Ramdohr (55) postulates that at the time of its alluvial deposition the detrital uraninite had a special refractoriness due to it being very young. The only aspect on which all agree is that the pay minerals are detrital. This unanimity in the midst of dissension recalls the one-mindedness with which the placerists have interpreted the mineralization as alluvial notwithstanding an absence of agreement on whether the host-rocks are continental, glacial, deltaic or marine.

It is doubtful whether any useful purpose is served by seriously reviewing these various hypotheses, unsupported by field evidence as they mostly are; but an excuse for this is to be found in the extent to which such views, if not contradicted, may be erroneously regarded as a sound foundation for future work. A recent example of this merits quotation. Louw and others have

lately postulated the existence of a reducing atmosphere in Precambrian times to explain the persistence of "detrital" uraninite and the presence of a high uranium:thorium ratio in the banket reefs, in this echoing a similar hypothesis of Lett (43) many years ago, adduced to favor survival of "detrital" pyrite. More recently Adams and Pliler (1) have maintained that the high uranium: thorium ratio in such sediments is indicative of the presence of a reducing atmosphere in Precambrian times. This circle of argument has validity only if the uranium mineralization is alluvial, and thus demands acceptance as a truism of the very point that is in dispute.

A brief review of some of the evidence for and against the notional reducing atmosphere has been given by the writer in earlier publications, where it is suggested that such a conception is incompatible with the existence of ferric iron ore horizons in the sediments of the Witwatersrand formation itself. Lately Geijer (28) has demonstrated that the sedimentary iron ores of Sweden point to the existence of an oxidizing atmosphere about 2,000 million years ago; and comparable conclusions for other periods of the Precambrian could be drawn from knowledge of the iron and manganese ores of every continent. Such deductions are by no means contradicted by conclusions arrived at from the ratio of radioactive elements in ancient sediments, provided the latter evidence is studied in full. Both in North America and South Africa a thorium-rich mineralization, entirely devoid of uranium minerals and sulphides, is to be found in sediments of the same age as the bankets and situated at no great distance from the mining fields. Thus in the Huronian quartzites of Michigan (67) there is to be found the most extensive mineralization of monazite (7.6%ThO_2, 0.20%U_3O_8) ever seen in an ancient sediment, the uranium:thorium ratio of 3:1 in the conglomerates at Blind River changing to 1:36 some 200 miles to the west. Similarly in the Mozaan quartzites of Swaziland (18), there are radioactive horizons with monazite, thorite, and zircon, but bearing neither uraninite nor sulfides. Comparable zircon-monazite associations have also been recorded as heavy residues from quartzites close to and roughly contemporary with the Algonkian bankets of Brazil (7). These thorium-rich mineralizations may be of hydrothermal origin, co-genetic with and perhaps zonal around the uraninite-gold-pyrite trinity; but accompanied as they are by grains of hematite, magnetite and ilmenite, they have every appearance of being normal detrital assemblages, the same as alluvials of present-day deposition. Whatever their origin, they convincingly dispose of the myth that detrital uraninite survived because of a reducing atmosphere.

The hypothesis of an atmosphere of carbon dioxide adduced to explain the survival of detrital uraninite is equally unsupported by the field evidence, for carbonate rocks are absent from the Witwatersrand sediments and indeed they are uncommon throughout the Precambrian of the world as a whole. The inadmissibility of this assumption is also manifest on considering the carbonate chemistry of uranium (49), for in the presence of carbonic acid uraninite is readily transformed to carbonate salts such as rutherfordine or sharpite.

Arguments based upon a non-actualistic Precambrian atmosphere may be confidently dismissed if it can be shown that conglomerates mineralized with pyrite, gold, and uranium are to be found in post-Proterozoic strata. One

not wholly unequivocal example is to be seen in the auriferous pyritic conglomerates of the Deadwood formation of Cambrian age, in the Black Hills of South Dakota. Here basal quartz-pebble beds, close to the well-known replacement ore-bodies of the Homestake mine, were at one time worked for gold. According to Lindgren (46) and some earlier authors, these conglomerates form "probably the best example of ancient placers"; but later work strongly favors the view that the gold is concomitant with pyritic replacements of Tertiary age (51). Age determinations suggest that throughout the Black Hills both Precambrian and Tertiary mineralization may be present (41). Recently uranium has been found, though not in payable quantity, in the auriferous Deadwood conglomerates (66); and this pyrite-gold-uranium association must therefore form either a placer accumulated under the normal oxidizing atmosphere of Cambrian times (a possibility discounted by earlier arguments) or a hydrothermal, (?) Tertiary, replacement. The latter view is supported by the presence of uranium mineralization in Ordovician and particularly Cretaceous sediments nearby. The Black Hills province, though not strongly mineralized, seems to form a structural link between the type of ore deposit seen in the Witwatersrand and Blind River, and the kind of occurrence seen in Northern Rhodesia and the Colorado Plateau.

In support of his hypothesis that the Witwatersrand conglomerates are of glacial origin, Wiebols (70) has attempted to show that the major reef horizons are underlain by tillites, that the reefs themselves were formed as lag deposits when these tillites were eroded by a transgressive sea, that the pay streaks are fossil esker or åsar, and that the erosion channels in the reefs are due to glacial scour. The uraninite is supposed to have been transported to the basin of deposition by ice, and to have survived only in those reefs subjected to a minimum of natural milling. Support for these views may be claimed in the reported presence of sparse tillites, and of dreikanter that might have been formed in polar deserts, within the Government Reef Series—though the attribution of a glacial origin to these strata dates from a time when tillites were "fashionable," and a reinvestigation is perhaps warranted. Against such suggestions, there is the overwhelming objection that in the Rand (as at Blind River) the payable conglomerates are typically oligomictic, the pebbles comprising solely vein quartz with subsidiary quartzite and chert, whereas glacial pebble-beds are characteristically the most polymictic of all common strata, with the greatest variety of rock types. Further, it is generally asserted (8, 2) that the economically important reefs are those that have received the maximum amount of natural milling, the antithesis of Wiebols' requirement. Again, since uraninite is found throughout a geosynclinal sequence of 35,000 feet, which from analogy with other geosynclines must have required upwards of 20 million years for its formation, this glacial hypothesis demands a succession of ice ages much more prolonged than any other known in geological history. And as no workable placer deposit of gold with uraninite has yet been discovered in Canada or Russia despite extensive alluvial prospecting in these arctic lands (6, 42), it is difficult to see how this hypothetical glacial derivation of the bankets materially strengthens the placerists' case. The weaknesses of the alluvial theory lie not so much in past studies of field

geology, so ably undertaken by generations of capable workers, as in interpretations of the fundamental geochemistry of the ores.

Ramdohr supposes that the Witwatersrand uraninite was very young at the time of its fancied alluvial deposition, this supposition being arrived at by an irrational deduction from published age determinations; and he further assumes that such young uraninite, derived from primary deposits appreciably less than fifty million years old, possesses a refractoriness otherwise quite unknown in this mineral. On this hypothesis young uraninite may accumulate in a placer deposit under conditions in which old uraninite could not survive! In furtherance of this view Ramdohr mentions a very young, supposedly refractory, uraninite (age thought to be about ten million years) from the Bergell Alps (33), which differs from the normal opaque mineral in having a brown-red translucency in thin splinters; and he also finds support in the observation that "a good octahedral cleavage" is to be seen in many of the Witwatersrand uraninite grains, this abnormal cleavage having been notionally induced in the young mineral at the time of formation of the conglomerates. None of these claims will stand examination. The Bergell uraninite (an occurrence in granite devoid of commercial interest) occurs heavily coated with yellow alteration products and is manifestly very far from refractory. The "typical octahedral cleavage fissures" (of which the three illustrations in Ramdohr's monograph speak for themselves) are to Liebenberg, from a study of 25,000 grains, no more than occasional "suggestions of an octahedral parting." In the writer's experience this indistinct parting is less evident in Rand material than in some of the hydrothermal uraninite of Shinkolobwe. It has already been noted by Rogers (57) in uraninite from pegmatites in Connecticut. As a criterion of alluvial deposition it is valueless.

Some geological considerations likewise rule out Ramdohr's hypothesis. The vertical distribution of uraninite ranges from the basal Dominion Reef upwards to the Black Reef. If the mineral were derived as detritus from very young granites and pegmatites, then the emplacement of these igneous rocks in masses of truly vast size must have preceded the deposition of the earliest sediments by no more than a few million years. Such a concept is surely contrary to all ideas of geosynclinal development. And since, as already emphasized, the deposition of these 35,000 feet of sediments must have taken at least 20 million years, during which period the uraninite would lose its refractoriness by ageing, one would expect the dominant mineralization to occur in the Lower Division (this, together with the Dominion Reef, supports two mines) rather than in the Upper Division (where, together with the Black Reef, some ninety mines are situated). Thus no support can be found for the idea of uraninite being refractory because of an extreme youth.

Next, there is Bain's contention (4) that the groundwaters in Precambrian times, antedating the existence of the first vascular plants on earth and supposedly preceding the formation of the earliest soils, were neither acid nor alkaline, but were exactly of pH 7 at which uraninite is insoluble. It is claimed that before the existence of a land flora the ground surface "was mantled with disintegrated rock and river water had the same neutral hydrion content as the Alpine streams." Evidence of the validity of this interesting conception is as

yet lacking. Such a view would be tenable if the Witwatersrand conglomerates exhibited in their pebble content that diversity of rock types which must have formed the parent land mass (a diversity such as is seen in Alpine streams), and if the quartzites contained a crop of those ferromagnesian minerals (as stable as uraninite under neutral conditions) to be expected as derivatives of an assemblage of rocks yielding chromite and zircon as ultimate resistates Since neither the variety of pebbles nor this diverse heavy-mineral assemblage is found, but since on the contrary the conglomerates and quartzites display less petrological variety than most post-Proterozoic analogues, the notion of stability of uraninite due to neutral groundwaters cannot be upheld.

But even if one or more of these heterodox supports to the placer hypothesis could be admitted, they one and all fail to explain the geochemical abnormalities of the bankets. In the Witwatersrand reefs the urania:thoria ratio is between 25:1 and 30:1, thorium being quite unimportant relative to uranium; and in the Blind River conglomerates the same ratio is around 3:1. In granitic rocks and pegmatites, however, the ratio of uranium to thorium has been found by many independent workers to average between 1:3½ and 1:4. Furthermore, the thorium is present in these rocks almost wholly within discrete radioactive minerals (monazite, thorite, etc.), which under any conceivable geological conditions have a survival rate certainly not less than that of uraninite. A detrital assemblage derived from granites or pegmatites cannot, therefore, fail to have an excess of thorium over uranium—and conversely an assemblage with uranium uniformly in large excess over thorium cannot be derived from granites and pegmatites. These deductions are so convincing that in a recent discussion they have brought Liebenberg (45, p. 249) close to jettisoning the views on the source of the uraninite that the placerist school has hitherto held. He says: "Many workers in the Witwatersrand field, including myself, favor granitic pegmatites as a source of the components of the banket; but the whole question involving the ratio of other radioactive minerals is changed if an ancient uraninite deposit similar to the one at Katanga [Belgian Congo] were situated in the area from which the erosion products were derived." Ramdohr (55, p. 41) concludes that the whole "detrital" assemblage was derived from the erosion of an infinite (*unendlich*) number of hydrothermal veins, probably from an array of veins of several different paragenetic types. Thus although a battery of so-called "proofs" has been produced by Liebenberg and others to show that the Rand uraninite is of a type restricted to granites and pegmatites and altogether distinct from the uranium mineralization of hydrothermal veins, recourse is necessarily made to the latter source of origin to keep the placer hypothesis alive.

Leaving aside the paramount geochemical problems, there is no great difficulty in envisaging the derivation of a placer mineralization, exhibiting great uniformity throughout thin conglomerate reefs of wide extent, from the denudation of a regional complex of feebly mineralized granites and pegmatites; but to derive the same uniform mineralization by alluvial processes from hydrothermal lodes is quite another matter. In the latter case the pay minerals must be distributed into the alluvium from what are little more than point sources; and a uniform distribution throughout reefs or throughout pay-

streaks many miles away could only be achieved if these sources—the hydrothermal veins—were very numerous and of like mineralogy. Ramdohr's suggestion that the sources of the mineralization were polygenic, with pyrite, arsenopyrite and gold derivative from auriferous quartz lodes, and uranium, cobalt, and nickel from polymetallic veins, is even more difficult to maintain in view of the sympathetic ratios of the pay minerals in the reefs.

It is manifest that the several departures from actualistic principles which geologists of the placerist school have adumbrated in necessary support of their views do not stand up to critical examination. If, therefore, the bankets do represent fossil placers, we must conclude that the placers were derived not from granites or pegmatites but from polymetallic veins; that the normal processes of oxidation and gossan formation over these sulfidic lodes, and the decomposition and comminution of the ore minerals during transportation, were inhibited by physico-chemical conditions that we can neither envisage nor explain; that these hypothetical lodes surrounded the basin of deposition in numbers quite unparalleled in any known mineral field; and that the tonnage of pay mineral discharged from the lodes into the alluvials, to give rise to ore and sub-ore alike, exceeded many hundred-fold that in the richest lode deposits exposed to-day. Acceptance of the hypothesis thus demands a suspension of the scientific judgement in favor of an article of faith, nourished not so much by evidence as by dogma.

THE EVIDENCE OF MINERAGRAPHY

At the present time the placer theory is sustained almost solely by the monographs of Ramdohr (55) and Liebenberg (44, 45) or the mineragraphy of the Witwatersrand ores. In these works it is claimed that the syngenetic origin of the deposits is conclusively demonstrated by the rounded shape of the contained uraninite grains. Both authors overlook an earlier statement by the present writer (15, p. 14) that "the rounded form of the uraninite grains in the Rand thucholite, which superficially might be taken as evidence of alluvial origin, can be matched exactly by grains from the hydrocarbons of fissure lodes." There is evidence that their studies have lacked due objectivity.

Liebenberg, for example, in an account (45, p. 159) of the well-crystallized monazite described in 1933 by Mendelssohn and Marland from the Sub-Nigel mine avoids the use of the critical word "hydrothermal" assigned to the occurrence by its discoverers. This mineral, which the present writer (16) has likened to the hydrothermal monazite in the gold-uranium ores of Shinkolobwe, is uncompromisingly dismissed as "an authigenic constituent of the conglomerate"—despite the absence of any previous record of authigenic monazite in sedimentary rocks.

Ramdohr's studies were based on "polished sections of 110 specimens . . . brought together at various periods from 1890 to 1953," many of the specimens being unlocalized. Despite a promise that "the author will express himself in the most cautious terms, using the indicative mood to describe observations and the subjunctive mood for possible (although in some cases *very* probable) explanations," he has no hesitation in extrapolating from the microscope to

the mine. Thus he claims repeatedly and unequivocally that uraninite and thucholite are restricted to the bottom of the reefs. "Uraninite entered the conglomerates as small detrital fragments and, owing to its weight, accumulated at the footwall." In this a conclusion that can reasonably be drawn, without field experience, from a few drawers of miscellaneous specimens—or is it rather a revelation of thinking conditioned by pre-conceived ideas? Ramdohr even casts doubt on an observation (by the Consulting Geologist!) that at Babrosco thucholite may be concentrated not solely at the base of the reef, but at the top, the middle, or the bottom. He does not refer to the detailed reports accompanied by full analytical data which Graton (30), Cowles (12) and many others have furnished to show that the 'rule' of basal concentration of gold in these reefs is as much honoured in the breach as in the observance. Liebenberg (45, p. 170) likewise states that "the highest concentration of uraninite grains occurs mainly in the lower portions of the conglomerate reefs"—although a few visits underground with a Geiger counter would have demonstrated that this generalization is far from true. The writer's own observations made in the latter way, coupled with published data on gold values, suggest that the distribution of gold and uranium throughout all these conglomerates is exactly paralleled by the distribution of heavy metals in coal seams(17)—there may be a concentration towards the base, in the middle, at the top, or right throughout, according to the channels preferentially taken by mineralizing fluids.

It is noted by Liebenberg that there is much uraninite present in the Witwatersrand reefs that does not have a rounded form but which occurs as veinlets and irregular patches in the matrix, in places invading and replacing quartz pebbles or pyrite. As this clearly cannot be of alluvial deposition he calls it "secondary uraninite," since he believes it to be derived from original detrital grains by reworking. A situation is thus created whereby all rounded particles of uraninite in the banket are automatically regarded as of primary, detrital origin, whereas uraninite (pitchblende) in any other shape or form is accepted as secondary or reworked. That reworking does occur in the banket reefs, giving rise to two or more generations of uraninite, was first demonstrated by Bowie and the writer (15) and has since been proven conclusively by age determinations (35, 36). Nevertheless, Ramdohr states that he has never seen two or more generations. "The author has searched very carefully for pitchblendes that are unmistakeably young . . . but without success. If such pitchblendes do exist, they can only play a *very* small part in view of their quantity and distribution."

Ramdohr makes another contradiction of the writer's work in discussing the source of the hydrocarbon gases that have been polymerized or condensed by the uraninite to form thucholite, this thucholite being one means whereby the uraninite is reworked. He states: "According to Davidson the 'coaly matter' is derived from stray methane from the Karroo coals. This view is not only improbable, but demonstrably incorrect." In 1951, reasons were given by the present writer for regarding the thucholite as predominantly of late hydrothermal age; but in 1953, on being informed of the widespread local opinion that the abundant hydrocarbon gases on the Reef originated in over-

lying Karroo coals, he suggested that much of the thucholite could well be of post-Karroo date. It was added: "If the derivation of the methane principally from Karroo strata is accepted, it becomes apparent that the two generations of pitchblende intimately associated with the hydrocarbon of the reefs must be of very diverse ages—one presumably quite old, the other as recent as post-Karroo." This inference has now been confirmed by the work of Horne (36), who has demonstrated from isotopic assays that some of the uraninite is as recent as 110 million years. It is indeed very probable that the thucholite has formed at many periods of time and may even still be forming; but Ramdohr's interpretation that organic matter, already polymerized, entered the Black Reef as detritus at the time of the reef's formation does not merit serious review.

Much confusion has arisen in the mineragraphic reports, particularly that of Liebenberg, by the usage of the essentially synonymous words pitchblende and uraninite. The Rand mineral is said to be "uraninite" and not "pitchblende"—and the placer hypothesis is therefore sustained by a widespread but quite erroneous belief that the latter is exclusively a hydrothermal mineral and the former a pegmatitic (and thus by derivation a detrital) one. This South African argument against a hydrothermal origin for the "crystalline uraninite" is invalidated by the observation that in every well-described instance where hydrothermal vein uranium is associated with noteworthy gold, such as Shinkolobwe (21), Goldfields (56) and Placer de Guadelupe (40), the uranium oxide is present, at least in part, as well-developed cubes and octahedra. Liebenberg (45, p. 244) has been at pains to chide the writer for his use of the term "pitchblende" for the "uraninite" present in the Carbon Leader of Blyvooruitzicht. Perhaps it is relevant to quote from his report (44, p. 78):

> That some *pitchblende*, closely associated with hydrocarbon, was deposited from solution is beyond doubt, as is clearly shown by veinlets and irregular patches of this mineraloid occupying fissures and cavities in specimens of massive hydrocarbon from the Ventersdorp Contact Reef (Western Reefs), and also in similar materials from the Carbon Leader (Blyvooruitzicht).

The oval and rounded particles of uraninite so characteristic of the South African thucholite as seen under the reflecting microscope were described by Bowie and the writer in 1951 as "colloidally dispersed pitchblende in blebs and similar forms indicative of a colloidal origin," in which there is to be seen "syneresis and ageing of the colloid system with late redistribution of pitchblende, sulphide, and gold in cracks." Analogies were drawn between the structures observed in banket "carbons" and those of thucholite from hydrothermal fissure veins. Ramdohr (55), however, contradicts these observations with the statement that the uraninite grains are detrital, showing none of the characteristics of colloidally generated pitchblendes. Liebenberg likewise concludes that "the minute grains of uraninite exhibit all the characteristics of a detrital mineral in appearance and manner of occurrence," and the syneresis or shrinkage structures so well exhibited in some of his illustrations are dismissed as brecciation cracks formed during metamorphism. We have

thus reached opposing conclusions from the same evidence. The implications of this crucial tenet of the placerist arguments are examined below.

In both mineragraphic studies, the authors attempt to bring their observations on the so-called "detrital" uraninite into agreement with the popular "modified placer hypothesis" for the gold. Liebenberg states (45, p. 118) that "the water-worn nature of fresh grains of uraninite is clearly evident. Oval grains predominate. Round grains are common whereas subangular or subhedral grains . . . are comparatively rare." On the other hand (p. 160) "Rounded and oval grains of gold, perfectly preserved, are only rarely encountered in the matrix of the banket. . . . Most of the gold is not detrital in its present form." In Ramdohr's work we read (55, p. 22) that "all the uraninite grains (of 2,000 examined) are *Gerölle* of varying sizes"; and (pp. 29–30) "It has long been admitted that the gold, or at least most of it, does not occur in forms such as those we are accustomed to see in placers. . . . The gold is certainly recrystallized." If we accept these observations we must therefore admit that throughout the supposed pseudohydrothermal transformations of the reefs and throughout their complicated metamorphic history, the uraninite, a mineral soluble in most geochemical environments, has persisted with its water-worn form quite unchanged, whereas gold, the paragon of chemical stability, has been so dissolved and redeposited that virtually no trace of its detrital origin remains.

The remarkable stability demanded of this "detrital" uraninite is evidenced in other ways. Ramdohr, who previously (54, p. 821) listed ilmenite and magnetite as typical of the Rand paragenesis, now shows that magnetite has very rarely been preserved and ilmenite only rarely. That detrital iron ores must have been initially present in the reefs in quantity proportional to the detrital chromite or garnet will be admitted by everyone, and that sulphidation of these oxide ores must have occurred during hydrothermal or pseudohydrothermal activities is likewise undeniable. But Ramdohr states that this pyritization of ilmenite occurred on such a vast scale that authigenic rutile was formed "everywhere in enormous quantities." Further, this rutile (not always being readily apparent) is said to have migrated considerable distances, even into the footwall, with sufficient concomitant reconstruction of the reefs that rutile needles penetrated the periphery of quartz pebbles. It is maintained that throughout these geochemical vicissitudes the uraninite grains preserved their pristine water-worn surfaces, victorious over the onslaughts of nature! But what was the chemical environment in which stable or refractory minerals like gold and rutile could migrate readily, and uraninite remain unattacked?

Another placerist argument advanced by the mineragrapher is that the uraninite is consistently associated with undoubted detrital minerals, showing "a tendency to be concentrated with smaller grains of higher specific gravity and larger grains of chromite and zircon of lower specific gravity" (45, p. 245). The only minerals present of higher specific gravity than the uraninite are platinoids and gold. But the platinoids have been seen in matrix only very rarely, and the gold is admitted to be "pseudo-hydrothermally reworked," its grain-size thus being quite irrelevant to these considerations. As indicated above, a uraninite-gold-platinum association is a typical hydrothermal one.

Further, Liebenberg (44, p. 82) notes that gold appears to show "a greater affinity for detrital uraninite than for other detrital constituents such as pebbles of quartz, zircon, and chromite." That detrital chromite and zircon should be found in the same parts of a reef as gold and uraninite is not at all contrary to hydrothermal ideas, for it is precisely these heavy minerals in more than ordinary concentration which would mark zones of scour possessing more than ordinary permeability.

The grain-size and well-sorted nature of the uraninite particles is likewise claimed as evidence of alluvial origin. Liebenberg (45) has estimated, from over 25,000 measurements, that "the average diameter of the uraninite grains in the Witwatersrand banket is about 75 microns." He shows that in the Kimberley Reef at East Daggafontein, 70 percent of the measured grains are more than 0.03 mm and less than 0.08 mm; and in many mines from 30 to 50 percent of the uraninite grains are less than 0.05 mm. The maximum size of grain recorded at all properties except Dominion Reefs, where the uraninite is slightly coarser, is under 0.2 mm. Compare these results with the findings of sedimentary petrologists. From pioneer studies on the rounding of sand-grains Ziegler (73) concludes that grains less than 0.75 mm in diameter cannot be rounded in water. Marshall (50) is of the opinion that grains less than 0.59 mm across diminish in size by solution rather than by abrasion; but Galloway (27) places the lower effective limit of abrasion by water at 0.05 mm. Pettijohn (53) suggests that there is a lower limit of rounding by abrasion near to 0.1 mm; and Twenhofel (65) believes that rounding of sand grains of dimensions below 0.5 mm involves extremely long tractional transportation. All these latter observations relate to quartz particles and they cannot be applied unreservedly to other minerals. Rounded grains of monazite, tourmaline, or xenotime as small as 70 microns certainly occur in the very finest fractions of well-worked beach sands. But before the rounded shape of even more minute particles of uraninite can be considered as "clear evidence of their water-worn nature," it would seem necessary to demonstrate that rounding by abrasion can occur at the sizes observed. Rounding by solution would be more readily admissible. But solution is necessarily denied by the placerists, for if solution took place the amount of uranium dissolved by the waters of the Witwatersrand cuvette would have been truly immense, and most of this uranium should have been adsorbed on the shaly sediments deposited in these waters. The fact that the Witwatersrand shales are among the least radioactive strata of the System is one of the most convincing contradictions of the placer theory.

Altogether the most surprising conclusion of the recent mineragraphic studies is the claim of Ramdohr that a large proportion of the pyrite entered the banket as detrital grains, thus revivifying the long-extinct conception that the buck-shot pyrite and pyrite "pebbles" are of alluvial deposition. It is categorically stated that "the explanation of rounded particles as replaced detritus is almost 100 percent nonsense!," but beyond this direct negation there is no discussion, or even mention, of the very relevant investigations of Horwood (37) and other early workers. Ramdohr finds that the pyrite is polygenic, and that much of it, including the buck shot, is a concentration of

detrital grains. Some, however, represents a replacement of itabirites and oolitic iron ores which were pyritized *before* erosion and deposition in the conglomerates. Some is a replacement of ilmenite, magnetite and other iron ores present in the "black sand" of the reefs. Some is concretionary, the concretions shortly antedating the alluvial gravels in which they later accumulated. Some is idiomorphic pyrite formed *in situ*, and some forms fissure fillings of relatively recent date. It is claimed that the detrital pyrite accumulated under a reducing atmosphere in which sulfur bacteria flourished. Liebenberg (45, p. 247) has "endeavoured to steer clear of the controversy concerning the origin of the pyrite," but he is prepared to accept detrital pyrite, and a reducing atmosphere, rather than give credence to hydrothermal views. Perhaps it is best to leave these claims to speak for themselves.

The diameter of the "detrital" pyrite grains is not mentioned by Ramdohr, but the pyrite *Gerölle* figured by him range from 0.05 mm to 0.5 mm. According to Young (71) the rounded pyrite in the Rand banket averages about 0.1 mm across. It is therefore of interest to refer to a study by Douglas *et al.* (22), who from ball mill tests conclude that during alluvial processes there is no appreciable rounding of pyrite grains less than 1 mm in diameter. Again some experimental demonstration seems to be called for before one can seriously entertain the view that grains of 100 microns diameter or less owe their rounding to abrasion.

In Canada the geologists charged with the rapid development of the Blind River field have been too busy with their immediate task to give much attention to fundamental problems of ore genesis; but here also, because of the remarkable uniformity in grade and distribution of the mineralization along parts of the conglomerate horizons, a theory of syngenetic deposition is favored in some quarters. As in the Witwatersrand, field evidence superficially favoring a detrital derivation of the radioactive minerals is flatly contradicted by geochemical thinking. Holmes (34), referring to the Pronto mine, observes: "It may be said with some reservation that high pyrite content will be accompanied by high uranium values"; but nevertheless he rather favors the conclusion that although the pyrite is undoubtedly hydrothermal, the uranium may well be alluvial. One of his main reasons for so doing is that at Blind River there are important developments of radioactive quartzites and radioactive grits that have as high a uranium content as the conglomeratic ores but which are devoid of pyrite. These mineralized quartzites occur where the conglomerates are locally absent from the succession, occupying the same stratigraphical horizons as the latter. But in no circumstance is it possible to envisage the alluvial accumulation of a great concentration of uranium minerals, even of refractory minerals, without these being associated with a vast excess of titaniferous iron ores. The absence of noteworthy ilmenite or titanomagnetite from these pyrite-free quartzites is therefore a clear indication that the uranium is not of detrital origin.

In the Blind River field, much of the uranium is reportedly present as the titanate brannerite, uraninite being believed to play a subordinate role; but in the Witwatersrand, brannerite has not been specifically recognized, even as a minor accessory of the ubiquitous uraninite. The recent mineragraphic

investigations have demonstrated, unwittingly, that this fancied difference between the two provinces does not exist. Apart from variations in the tenor of the pay metals, the two fields are, mineralogically, almost completely alike. Perhaps this fact, hitherto unrecognized, is the most noteworthy contribution of these studies.

In explanation of this point it should be emphasized that the diagnosis of the dominant uranium mineral at Blind River as brannerite has been difficult to reconcile with the chemical behavior of the ore which, although less easily brought into solution than uraninite or pitchblende, is appreciably less refractory than the brannerite of quartz veins, granites and pegmatites. This behavior can be explained by the observation that nearly all the Blind River mineral is much decomposed to a mixture of felted anatase (leucoxene) and pitchblende or thorogummite. The unheated mineral gives the X-ray diffraction pattern of anatase, and a brannerite pattern is not obtained until after strong heating in the absence of air. Some of the ore contains no brannerite at all, all the uranium being present as particles of pitchblende or uraninite (100 microns in average cross section), in places forming grains of angular or subrounded shape, in other places crystals of cubic or octahedral habit, the cores of the crystals commonly being replaced by quartz (31, 38, 64).

In his study of the Witwatersrand ores Ramdohr has determined the presence of rare grains of a radioactive titaniferous mineral, tentatively identified as brannerite or davidite, which is much decomposed to a white aggregate of titanite, rutile or leucoxene, associated with considerable "radiogenic" galena. He also refers at some length (55, p. 22) to the presence of "enormous numbers" of so-called "pitchblende ghosts," consisting of an aggregate of an unidentified dull white material similar to leucoxene, again associated with abundant fine galena. Liebenberg (45, p. 156–8) describes identical felted aggregates as uraniferous leucoxene, which he suggests was formed by the alteration of a detrital, uraniferous, sphene. There can be little room for doubt that this "leucoxene" is precisely the same material as is recognized by the Canadian mineralogists to be altered brannerite. Ramdohr's conclusion that these titaniferous "ghosts" are relics of detrital pitchblende fragments that failed to survive the processes of lithification must be dismissed, since this in no way explains the source of the titanium.

In a recent, imaginative, contribution Holmes (34) has suggested that the brannerite at Blind River was deposited as a detrital mineral; and that after consolidation of the sediments hydrothermal solutions, emanating from nearly granites, permeated the conglomerate horizons, depositing pyrite and altering the brannerite to uraninite. Such an explanation may well be seized upon in South Africa now that the former widespread existence of brannerite in the Witwatersrand has been demonstrated. As Graton (30) so aptly said, "the resiliency of the placer theory is remarkable, for when it does crash into one unyielding mass of fact, it bounds off, recasts itself appropriately, and gayly rushes forward to a new collision, undaunted by sad experience."

THE AGE OF THE MINERALIZATION

In the hope that the vexed question of the origin of the ores might be solved by absolute dating of the mineralization, investigations have been carried out by several workers (35, 47, 63, 68) on the isotopic composition of the uraninite and galena from the Witwatersrand and Blind River bankets. Unexpectedly these mass spectrographic studies have posed many more problems than they have solved. One noteworthy discovery is that in both fields some of the galena present contains a very high tenor of the radiogenic isotopes. Since other highly radiogenic galenas are known only in pitchblende lode deposits in which re-working has occurred (26, 56), this strongly suggests that re-working (solution and redeposition) may have been an important factor in determining the mineralogical make-up of the reefs as seen to-day.

TABLE 1

ISOTOPIC ANALYSES OF GALENA LEADS

Locality	^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb	Reference
Witwatersrand:					
I. South Roodeport	1.00	16.39	15.40	32.21	(47)
II. East Geduld	1.00	18.35	16.34	34.48	(47)
III. Freddies	1.00	38.5	19.46	32.96	(47)
IV. Sub Nigel	1.00	29.9	19.8	38.8	(47)
V. Sub Nigel	1.00	61.83	24.5	40.82	(35)
Blind River:					
VI. Algom: 1,500′ above ore	1.00	17.11	15.96	36.35	(68)
VII. Algom: ore zone	1.00	34.00	15.08	44.26	(68)
VIII. Algom: cross fracture in ore zone	1.00	59.49	18.61	52.49	(68)

Isotopic analysis of eight samples of galena from the Witwatersrand and Blind River has given the following results, which in some cases have been confirmed, within the limits of experimental error, by check assays carried out by two or more mass-spectrographic laboratories.

The variation in composition is enormous. If the galena of South Roodeport, with the lowest content of radiogenic isotopes, is taken as representative of the average "common" lead uniformly distributed throughout the Witwatersrand field at the time of its initial (alluvial or hydrothermal) mineralization, then a later addition of close on fifty percent of radiogenic lead becomes necessary to provide a galena with the composition of that recorded from Sub-Nigel (analysis V). A similar addition is necessary to account for the isotopic composition of the galena from a cross-fracture at Algom (analysis VIII). There would seem to be two ways only in which this localized radiogenic enrichment could have occurred—either by leakage of the gaseous phases radon, actinon, and thoron during the radioactive disintegration of the uraninite or brannerite, or by reworking of the uraninite or brannerite, involving partition and redistribution of the radiogenic lead. Since it has been shown experimentally (35) that the radon leakage is small, the hypothesis of reworking thus becomes the sole tenable postulate. It will be noted that the galena at Blind River is appreciably richer in ^{208}Pb (relative to ^{206}Pb) than

those of the Witwatersrand, a circumstance in line with the greater richness in thorium of the Blind River ores.

The two analyses (IV and V) of galena from Sub-Nigel relate to two different concentrates prepared from precisely the same sample. This parent sample was itself a concentrate, consisting of uraninite (sp. gr. 7.6) contaminated with galena (sp. gr. 7.5) and assaying 63.0 percent U_3O_8, which had been laboriously prepared from the crude ore of the Main Reef in the laboratories of New Consolidated Gold Fields Ltd. By further beneficiation the Geological Survey of South Africa produced from this a galena (IV) containing "less than 0.6 percent U_3O_8" and a uraninite with 66.9% U_3O_8, and the Geological Survey of Great Britain produced a galena (V) containing "less than 0.1 percent uraninite" and a uraninite with 72.8% U_3O_8, a residue of uraninite-galena middlings being left in each case. The leads of these two galena concentrates differ in mean mass number by as much as 0.59; and one cannot avoid the surprising conclusion that this fractionation must be attributable to the differing amounts of physical beneficiation that the samples have received. It follows that the discrete particles of galena present in the reef at any one locality may vary considerably in isotopic composition; and as a corollary to this conclusion one must accept that in the reworking of the ores the movement of the metals has been restricted to a limited radius (perhaps no more than a centimeter or two) without general diffusion throughout the reef as a whole.

Many of the samples of Witwatersrand uraninite that have been examined by means of the mass spectrograph have been heavily contaminated with galena of unknown isotopic composition, thus vitiating conclusions that have been drawn regarding the age of the mineralization; but in the following table a list is given of what appear at first sight to be the more acceptable age determinations, together with recent determinations of the age of the ores from Blind River. Ages based on the ^{208}Pb:Th ratio are omitted, in view of the low thoria content of the ores.

Of the above determinations, analyses I, II and III (Sub-Nigel) were executed by different laboratories on fractions of the same sample, and therefore demonstrate the measure of agreement obtained by different workers, each with his own techniques. Analysis XI (West Rand Consols) is of a uraninite specially picked out under the ore microscope as representative of reworked mineral of relatively late age. The "best" age of this reworked uraninite has been shown elsewhere to be 110 m.y. (36).

The remarkably low ages reported for the Pronto mineralization relative to that of Algom (63, 68) is most surprising, for these two mines exploit precisely the same reef of conglomerate and from the field evidence there can be no doubt whatever that the two ores are cogenetic. One is tempted to postulate that the samples analyzed from Pronto (but not necessarily all the Pronto ore) have undergone a relatively late reworking, furnishing a "younger" uraninite together with a galena enriched in radiogenic isotopes.

With but rare exceptions, the general pattern of these age determinations is a sequence $^{206}Pb:^{238}U < ^{207}Pb:^{235}U < ^{207}Pb:^{206}Pb$. This sequence is the reverse of that seen in most age determinations based on the mass-spectro-

graphic study of uraniferous monazite, in which the incompatibility of the various ratios may be explained by leaching of uranium; but it is identical with the pattern of apparent ages reported from other provinces where uraninite or pitchblende is disseminated through sedimentary rocks, particularly the Colorado Plateau (62). The same pattern is also to be seen in apparent ages derived from many isotopic studies of vein pitchblende, and it is further apparent in investigations of many pegmatitic uraninites, notably those of Karelia (3). The reason for this consistent discrepancy between the ap-

TABLE 2

AGE DETERMINATIONS BASED ON URANINITE

Locality	Uranium content, %	$\frac{^{206}Pb}{U}$	$\frac{^{207}Pb}{U}$	$\frac{^{207}Pb}{^{206}Pb}$	Analytical laboratory
		Million years			
Witwatersrand:					
I. Sub-Nigel	61.75	1,352	1,652	2,056	Harwell (35)
II. Sub-Nigel	61.75	1,337	1,648	2,070	Toronto (35)
III. Sub-Nigel	61.75	1,328	1,593	1,965	Columbia (35)
IV. Sub-Nigel	57.3	1,612	1,875	2,215	Johannesburg (47)
V. Sub-Nigel	54.1	1,602	1,861	2,200	Johannesburg (47)
VI. Sub-Nigel	54.0	1,566	1,864	2,230	Johannesburg (47)
VII. Freddies	55.7	1,128	1,456	2,000	Johannesburg (47)
VIII. Marievale	53.5	1,304	1,595	2,035	Johannesburg (47)
IX. Wit Nigel	51.1	1,182	1,443	1,900	Johannesburg (47)
X. Blyvooruitzicht	49.5	1,825	1,913	2,020	Johannesburg (47)
XI. West Rand Consols	74.69	117	130	378	Harwell (36)
Blind River:					
A. Algom (Quirke)	*	1,850	2,060	2,250	Washington (63)
B. Algom (*)	43.8	1,170	1,300	1,400	Ottawa (68)
C. Pronto	48.3	630	600	590	Ottawa (68)
D. Pronto	*	340	520	1,400	Washington (63)
E. Pronto	*	440	600	1,250	Washington (63)
F. Pronto	*	400	570	1,350	Washington (63)

* Data not available.

parent ages arrived at from the different isotopic ratios has been sought by Stieff and Stern (62) and by Horne and the writer (35). The former workers conclude that the discrepancy may most reasonably be explained by the introduction of old radiogenic lead at the time of the initial mineralization, this old radiogenic lead being found not only in galena but also in pyrite and uraninite. The latter attribute the age pattern to reworking of the uraninite into two or more generations.

In earlier discussions of these age problems all workers, including the writer, have assumed that the discrepancy in apparent ages can be accounted for by a single simple explanation; but it is now clear that this assumption is far from valid. The occurrence of local reworking, in places on an extensive scale, is amply substantiated; but the common presence within non-uraniferous sulphide ore bodies such as Sudbury and Noranda (25) of accessory galena

enriched in radiogenic isotopes strongly suggests that old radiogenic lead may have been a significant component of the primary mineralization of the bankets. Age determinations may therefore be complicated (a) by the presence of two or more generations of uraninite; (b) by the presence of old radiogenic lead; (c) to a small degree only, by radon leakage.[1] It has thus become difficult to place any reliance on the apparent ages recorded for these banket ores. In the Witwatersrand, if old radiogenic lead is absent, the minimum age of the mineralization must be around 2,000 m.y., but if old radiogenic lead is present the ores can be very much younger, not impossibly even as young as those of the Congo-Rhodesian Copperbelt (620 m.y.). Similarly for the Blind River field, it has been seriously suggested (63) that despite their great apparent age the ores are "probably not older than Paleozoic."

Reflections on the source of this old radiogenic lead inspire some thoughts on the origin of the ores. Mineralization bearing a widespread enrichment in ^{206}Pb and ^{207}Pb can be explained solely by a regional regeneration of pre-existing uranium, most probably present not as discrete mineral but rather as a very dilute dispersion throughout a great thickness of sediments or gneisses. The motive force for the concentration and redistribution of this uranium, radiogenic lead, and associated metals must presumably be sought in the processes of orogeny and granitization.

THE SOURCE OF THE PAY METALS

The evidence that the metals contained in the banket reefs are epigenetic to the reefs themselves is overwhelming; and it therefore becomes of interest to consider whether these ore deposits are epigenetic to the geosyncline as a whole, or whether they arise from mobilization and redistribution of the metals originally present in the geosyncline at the time of deposition of the sediments. In other words, one must decide whether the metals derive directly as emanations from the granitization occurring towards the close of the active history of the geosyncline, or whether they have been concentrated in the more permeable conglomerate horizons by some form of "sweating-out" or lateral secretion from the surrounding strata.

An answer to this question could readily be found if, in addition to chemical assays on ore-bearing horizons, we had analytical information on the normal strata throughout the whole geosynclinal sequence. Unfortunately, however, mining companies show little interest in strata that are of no commercial value; and their customary methods of assay perhaps lack the sensitivity necessary to provide precise data on so-called "traces," solely of geochemical interest. It has become of fundamental interest to know whether the normal quartzites and arkoses of the Witwatersrand and Blind River are significantly richer in gold, uranium, and pyrite than are the arenites of geosynclines that do not contain ore deposits. Although quantitative data are lacking, there are some lines of evidence that suggest this is the case.

First, there is the evidence of gamma logging of boreholes. Radioactivity

[1] Recent work by Starik *et al.* (60a) demonstrates that up to about 400° C. the loss of radon from uraninite is small (1–2%) and virtually unaffected by temperature.

logs of borings through the Witwatersrand System have been published by Simpson (58, 59, 60); and although these give no precise quantitative measurement of the uranium content of the strata, they do show clearly that the arenaceous beds are not less and generally more radioactive than the argillaceous ones. Similar conclusions have been drawn from surface radioactivity surveys over the outcrop of the Mozaan Series of Swaziland (5). Since in all normal stratigraphical sequences argillites are more radioactive than arenites, we have here a surprising abnormality; and it is difficult to account for this abnormality by variations in the content of ^{40}K, for one would expect the shales to be the richer in potash. One must therefore conclude that the sandy strata in the Witwatersrand have been epigenetically enriched in uranium.

Second, there is evidence from the gold and pyrite content of the quartzites. Exceptionally local developments of these rocks, both in South Africa and Canada, are sufficiently enriched in gold or uranium, with or without pyrite, to form ore; but little has been published on the gold or pyrite content of the so-called "barren" beds. A study conducted by Macadam (48) on 4,000 feet of borehole core, with three or four assays per foot, resulted in the conclusion that:

> Very little gold was found in any of the quartzite layers and where gold was present, including traces to ½ dwt. per ton, pyritic seams were contained in them with some scattered grits and pebbles. Though one might not expect gold in the quartzites, it was quite surprising to find that the quartzites were almost devoid of gold. . . . In the quartzites separating the pyritic seams and reefs the quantity of pyrite is not great. Where the reefs contained 3 to 10 percent of pyrite, the quartzites contained as little as ¼ to ½ percent. In some of the quartzite layers up to 3 percent was present, but these layers proved to vary very much in pyrite content.

It seems probable that a "trace" of gold determined in the routine work of a mine assay office 25 years ago represents a significant measurable quantity to the academic geochemist; and Macadam's work perhaps suggests, not that the quartzites are "almost devoid of gold" (a turn of phrase conditioned by commercial values) but that these rocks contain appreciably more gold and pyrite than would be found in any similar sequence of "normal" strata. Although more data are very desirable, there is some reason to think that the so-called "barren" quartzites of the Witwatersrand are much richer in gold than the sandstones of other geosynclines.

Third, the high degree of mineralization in the bankets suggests a source for the uranium and the gold from without the geosynclines. The Main Reef of Blind River, weighted together with immediately overlying subsidiary conglomerates, has an overall content of around 0.09 percent U_3O_8 over an aggregate thickness of about 20 feet. Within this thickness there is the same content of uranium as one would find in a thickness of 5,000 feet of average granite or, allowing for loss by solution, within a still thicker pile of sediments derived from granite. In the Witwatersrand a single intersection at Rietkuel assaying 229 in.-lb has the same uranium content as 2,000–3,000 feet of granite. Again, a single payable reef in South Africa with an average of 200

in.-dwt. of gold contains in itself as much gold as 3,000 feet of average granite, without taking into consideration any other payable reefs or any mineralization of sub-ore grade. If, as concluded above, the "barren" quartzites contain at least as much gold and uranium as normal sandstones, it cannot but be agreed that these elements are epigenetic not only to the reefs but to the System as a whole.

A study of special interest in connexion with this last point has been undertaken by Duhoux (23) on the distribution of gold in the Kilo-Moto district of the Belgian Congo. Here the precious metal is worked from alluvials and from a great many quartz veins cutting schists, quartzites, and itabirites of Kibalien (Algonkian) age, these quartz veins being considered to be contemporary with a period of metasomatic granitization of the Kibalien. Duhoux's study furnishes 820 analyses of the gold content of both the Kibalien rocks and the granites, and demonstrates that: (a) of 141 samples of granite, 94 percent are devoid of gold and 6 percent contain ponderable quantities; and (b) of 679 samples of Kibalien, only 8 percent are devoid of gold, 23 percent contain traces, and 69 percent ponderable amounts. The distribution of values is as follows:

Tenor of Au, gm/ton	Granite (141 samples)	Kibalien (679 samples)
Nil	94%	8%
Trace	—	23%
0.05–0.25	4%	50%
0.25–0.50	—	14%
0.50–0.80	—	3%
1	1%	2%
>1	<1%	<1%

Duhoux infers that the gold is related to migmatic (but not to "mobilized") granite, since the exploitable deposits are commonly found close to zones of granitization; but he considers that the source of gold is not so much the granite itself as the pre-existing rocks that have been metasomatically transformed, the processes of granitization leading to a concentration and redistribution of the metallic elements on an enormous scale. *"Le front géochimique de granitisation chasse littéralement l'or devant lui."* This conclusion is in keeping with the well known concentration of gold, both in the form of disseminated and quartz-lode deposits, within the roof-pendants and other relics of ungranitized schist throughout the African shield (notably in West Africa and Southern Rhodesia), rather than in the granitized rocks themselves. The same distribution pattern is seen in the auriferous schists, quartzites, and conglomerates of parts of Siberia (20, v. iii, p. 515–522).

There are no firm grounds for the extrapolation of these views to the Witwatersrand and Blind River; and the hypothesis that the gold-uranium-sulphide mineralization in these two mining fields may be linked to a period of granitization in the late history of the geosynclines is at present no more than speculation. In comparing the two fields, however, it will be noted that the successions of strata in the Transvaal and in Ontario exhibit similarities so striking that they may well be more than coincidences. The Huronian and the Witwatersrand sediments alike are predominantly arkoses, quartzites, and itabirites with subordinate conglomerates and grits, which unconformably

overlie an ancient Basement of granite and gneiss. Both systems are succeeded by a great thickness of basic rocks—the Huronian by the basic sills and lavas of the Keweenawan, the Witwatersrand by the Ventersdorp Volcanic Series. In both provinces the epigenetic introduction of uranium seems to have post-dated this prolonged volcanic episode—in the Witwatersrand because mineralization is locally well developed in the Black Reef, which unconformably overlies the Ventersdorp lavas, in Ontario because Keweenawan dikes have formed structural controls (at Camray, Ranwick and elsewhere) for pitchblende veins which, according to apparent age data, are more likely than not coeval with the mineralization in the conglomerates. In South Africa the mineralization apparently dates from the period of post-Transvaal earth movements which gave rise to the Vredefort and other domes, accompanied by the Bushveld granite, alkalic plutons, and nepheline-syenite dykes. In Canada it may be linked to the Penokean orogenesis and the Killarnean granites of Sudbury and elsewhere, presumably contemporaneous with the nepheline-syenites and uraniferous pegmatites of the Grenville province since these agree in apparent dating with the post-Keweenawan pitchblende veins.

It is possible to carry speculation much further. May it not be, for example, that the Bushveld Complex with its sulfide mineralization stands in the same geochronological and geochemical relationship to the Witwatersrand as does Sudbury to Blind River? Are we right in regarding as syngenetic the banded ironstones and itabirites that form unexplained regional concomitants of gold deposits in so many parts of the world—or is the iron an epigenetic derivative of the complex cookery of granitization? Should we view the great mining fields providing the silver of Cobalt, the nickel of Sudbury, the uranium of Blind River, the iron of the Mesabi range and the copper of the Michigan Peninsula as basically cogenetic, springing from the same metalliferous font—and if so, what was the mechanism in the depths of an orogenic belt whereby fractionation of the elements took place? Perhaps these questions will never be answered. But it is worth while asking them if in a search for knowledge new ore fields are discovered. Useful as the placer hypothesis may have been in guiding exploration within a circumscribed area, it has provided no satisfactory basis for the search for new mineral provinces. A trend of thought that links more closely to orogenic conditions those geochemical abnormalities that we know as ore deposits may in the course of time greatly enrich the resources of mankind.

UNIVERSITY OF ST. ANDREWS,
ST. ANDREWS, SCOTLAND,
April 9, 1957

REFERENCES

1. Adams, J. A. S., and Pliler, R., 1956, Geochemistry of the actinides as a possible clue in interpreting the development of the earth's atmosphere: Geol. Soc. America, Bull., v. 67, p. 1663 (abstract).
2. Antrobus, E. S. A., 1957, The origin of the auriferous reefs of the Witwatersrand System: Geol. Soc. South Africa Trans., v. 59 (for 1956).
3. Avdzeiko, G. V., 1955, Rol' izotopnogo analiza svintza v opredelenii geologicheskogo vozrasta. Trudy III Sessii Komissii po opredeleniyu absolyutnogo vozrasta geologicheskikh formatzii: Academy of Sciences, Moscow, p. 153–162.
4. Bain, G. W., 1956, Contribution to discussion in Liebenberg, 1956: 236–240.

5. Beer, K. E., 1954, Report on car-borne radioactivity surveys in the Bechuanaland and Swaziland Protectorates. Atomic Energy Division, Great Britain Geol. Survey Rept. 158, 21 p.
6. Bilibin, Yu. A., 1956, Osnovy geologii rossypei (3rd ed.): Academy of Sciences, Moscow, 463 p.
7. Branco, J. J. R., 1956, Conglomerado do Samburó: Inst. Pesquisas Radioactivas, Univ. Minas Geraes, pub. 8, 10 p.
8. Brock, B. B., 1954, A view of faulting in the Orange Free State: Optima, v. 4, p. 5–17.
9. Cavaca, R., 1956, Uranium prospecting in Portugal: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 183–188.
10. Chew, R. T., 1956, Study of radioactivity in modern stream gravels as a method of prospecting: U. S. Geol. Surv. Bull. 1030-E, p. 145–169.
11. Cousins, C. A., 1957, The value distribution of economic minerals with special reference to the Witwatersrand gold reefs: Geol. Soc. South Africa Trans., v. 59 (for 1956). p. 95–122.
12. Cowles, E. P., 1931. Notes on the distribution of gold in the reef . . . : Geol. Soc. South Africa Trans., v. 34, p. 71–80.
13. Dana, J. D., 1854, A system of mineralogy (4th ed.): New York and London.
14. Davidson, C. F., 1947, Uranium and thorium in the tin deposits of Siam: Atomic Energy Division, Great Britain Geol. Survey Rept., 25 p. (unpublished).
15. ——, and Bowie, S. H. U., 1951, On thucholite and related hydrocarbon-uraninite complexes, with a note on the origin of the Witwatersrand gold ores: Great Britain Geol. Survey Bull., 3, p. 1–19.
16. ——, 1953, The gold-uranium ores of the Witwatersrand: Mining Mag., v. 88, p. 73–85.
17. ——, and Ponsford, D. R. A., 1954, On the occurrence of uranium in coals: Mining Mag., v. 91, p. 265–273.
18. ——, 1955, *in* Sum. Progr., Great Britain Geol. Survey for 1954, p. 70.
19. ——, 1955, The mineralization of the Witwatersrand: Mining Mag., v. 92, p. 152–6.
19a. ——, and Cosgrove, M. E., 1955, On the impersistence of uraninite as a detrital mineral: Great Britain Geol. Survey Bull., 10, p. 74–80.
20. De Launay, L., 1913, Gites minéraux et métallifères (3 vols.): Paris and Liège.
21. Derriks, J. J., and Vaes, J. F., 1956, The Shinkolobwe uranium deposit: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 94–128.
22. Douglas, G. V., et al., 1956, Some observations on syngenetic ores: Econ. Geol., v. 51, p. 427.
23. Duhoux, P. V., 1950, La pétrogenèse et la métallogenèse du domaine minier de Kilo-Moto: Ann. Soc. Géol. Belg., v. 73, p. M 171–244.
24. Eilertsen, D. E., and Lamb, F. D., 1956, A comprehensive report of exploration by the Bureau of Mines for thorium and radioactive black mineral deposits: U.S.A.E.C. Rept. RME-3140, 46 p.
25. Farquhar, R. M., and Cumming, G. L., 1954, Isotopic analyses of anomalous lead ores: Royal Soc. Canada Proc. and Trans., v. 48, p. 9–16.
26. Faul, H., 1954, Nuclear geology: New York & London.
27. Galloway, J. J., 1919, Rounding of sand grains by solution: Am. Jour. Sci., v. 47, p. 270–280.
28. Geijer, P., 1956, Pre-Cambrian atmosphere: evidence from the Pre-Cambrian of Sweden: Geochimica Acta, v. 10, p. 304–310.
29. Geological Survey of Japan, 1956, Natural occurrence of uranium and thorium in Japan: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 174–5.
30. Graton, L. C., 1930, Hydrothermal origin of the Rand gold deposits: Econ. Geol., v. 25, supplement, 185 p.
31. Hart, R. C., Harper, H. C., et al., 1955, Uranium deposits of the Quirke Lake trough, Algoma district, Ontario: Canadian Inst. Min. Metallurgy Trans., v. 58, p. 126.
32. Hawley, J. E., and Rimsaite, Y., 1953, Platinum metals in some Canadian uranium and sulphide ores: Am. Mineralogist, v. 33, p. 463–475.
33. Hirschi, 1925, Schweizerische Pechblende, ihr Radium- und Thoriumgehalt: Schweizer. Min. Pet. Mitt., v. 5, p. 249.
34. Holmes, S. W., 1956, The Pronto Mine—geology: Western Miner, v. 29, p. 121.
35. Horne, J. E. T., and Davidson, C. F., 1955, The age of the mineralization of the Witwatersrand: Great Britain Geol. Survey Bull., 10, p. 58–73.
36. ——, 1957, Age of a late uraninite from the Witwatersrand: Great Britain Geol. Survey, Age Determination Rept. 2, (mimeographed).
37. Horwood, C. B., 1917, The gold deposits of the Rand: London, 393 p.
38. Joubin, F. R., 1954. Uranium deposits of the Algoma district, Ontario: Canadian Inst. Min. Metallurgy, Bull., v. 57, p. 431–437.

39. Kayman, S., 1954, Mineralogy of a uranium ore from Pronto Uranium Mines Ltd.: Rept. SR 218/54, Mines Branch, Ottawa (Unpublished).
40. Krieger, P., 1932, An association of gold and uraninite from Chihuahua, Mexico: Econ. Geol., v. 27, p. 651–660.
41. Kulp, J. L., et al., 1956, Age of the Black Hills gold mineralization: Geol. Soc. America, Bull., v. 67, p. 1557.
42. Lang, A. H., 1952, Canadian deposits of uranium and thorium: Canada Geol. Surv., Econ. Geol. Ser. 16, 173 p.
43. Lett, S. J., 1917, Contribution to discussion in Horwood, 1917.
44. Liebenberg, W. R., 1954 (for 1948), Rare minerals in the banket of the Witwatersrand system: U.S.A.E.C. Rept. NP-3992, 141 p. (Unpublished).
45. ——, 1956, The occurrence and origin of gold and radioactive minerals in the Witwatersrand. Trans. Geol. Soc. S. Africa, v. 58 (for 1955), p. 101–254, pl. xv–xxxviii.
46. Lindgren, W., 1919. Mineral deposits, 2nd edition. New York & London.
47. Louw, J. D., 1955, Geological age determinations on Witwatersrand uraninites using the lead isotope method: Geol. Soc. South Africa Trans., v. 57 (for 1954), p. 209–230.
48. Macadam, P., 1931, The distribution of gold and carbon in the Witwatersrand bankets: Geol. Soc. South Africa Trans., v. 34, p. 81.
49. McClaine, L. A., Bullwinkel, E. P., and Huggins, J. C., 1956, The carbonate chemistry of uranium: Peaceful Uses of Atomic Energy (U.N.O.), v. 8, p. 26–37.
50. Marshall, P., 1929, Beach gravels and sands: Trans. New Zealand Inst., v. 60, p. 324–365.
51. Noble, J. A., 1950, Ore mineralization in the Homestake gold mine, Lead, South Dakota: Geol. Soc. America Bull., v. 61, p. 245.
52. Ostle, D., and Taylor, J., 1954, Notes on the occurrence of uranium and thorium in the Fort Victoria mining district, Southern Rhodesia: Great Britain Geol. Survey, Atomic Energy Division Rept. 165, 17 p.
53. Pettijohn, F. J., 1949, Sedimentary rocks: New York.
54. Ramdohr, P., 1950, Die Erzmineralien und ihre Verwachsungen: Berlin, 827 p.
55. ——, 1955, Neue Beobachtungen an Erzen des Witwatersrands in Südafrika und ihre genetische Bedeutung: Abh. Deutsche Akad. Wissensch., Berlin, Math.-Naturw. Kl., 1954, no. 3, 43 p., 33 pl.
56. Robinson, S. C., 1955, Mineralogy of uranium deposits, Goldfields, Saskatchewan: Canada Geol. Survey, Bull. 31, 128 p.
57. Rogers, A. F., 1947, Uraninite crystals with a new form from Portland, Connecticut: Am. Mineralogist., v. 32, p. 83.
58. Simpson, D. J., 1952, Some results of radioactivity logging . . . : Geol. Soc. South Africa Trans., v. 54 (for 1951), p. 99–133.
59. ——, 1953, Correlation by means of radioactivity logging . . . : Geol. Soc. South Africa Trans., v. 55 (for 1952), p. 33–52.
60. ——, 1953, Correlation of the sediments of the Witwatersrand system . . . by radioactivity logging: Geol. Soc. South Africa Trans., v. 55 (for 1952), p. 133–152.
60a. Starik, I. Ye., et al., 1955, *in* Byulleten Komissii po Opredeleniyu Absolutnogo Vozrasta Geologicheskikh Formatzii: Moscow (Academy of Sciences), no. 1, p. 33–38.
61. Steacy, H. R., 1953, An occurrence of uraninite in a black sand: Amer. Mineralogist, v. 38, p. 549–550.
62. Stieff, L. R., and Stern, T. W., 1956, The interpretation of the . . . age sequence of uranium ores: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 540–546.
63. ——, and ——, et al., 1956, Preliminary age determinations . . . from Blind River area, Ontario: Geol. Soc. America Bull., v. 67, p. 1736 (abstract).
64. Traill, R. J., 1954, A preliminary account of the mineralogy of radioactive conglomerates in the Blind River region, Ontario: Canadian Min. Jour., v. 75, p. 63.
65. Twenhofel, W. H., 1950, Principles of sedimentation: New York.
66. Vickers, R. C., 1954, Occurrence of radioactive minerals in the Bald Mountain gold-mining area, Northern Black Hills, South Dakota: U. S. Geol. Surv. Circ. 351, 8 pp.
67. ——, 1956, Geology and monazite content of the Goodrich quartzite, Palmer area, Marquette County, Michigan: U. S. Geol. Surv. Bull. 1030-F, p. 167–185.
68. Wanless, R. K., and Traill, R. J., 1957, Age of uraninites from Blind River, Ontario: Nature (London), v. 178, p. 249.
69. White, M. G., 1956, Uranium in the Serra de Jacobina, State of Bahia, Brazil: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 140–142.
70. Wiebols, J. H., 1956, A suggested glacial origin for the Witwatersrand conglomerates. Geol. Soc. South Africa Trans., v. 58 (for 1955), p. 367–382.
71. Young, R. B., 1917, The Banket: London, xv + 125 p.
72. Yun, T. S., 1956, Occurrence of uranium and thorium in South Korea: Peaceful Uses of Atomic Energy (U.N.O.), v. 6, p. 176–7.
73. Ziegler, V., 1911, Factors influencing the rounding of sand grains: Jour. Geology, v. 19, p. 157–191.

REFLECTING CURVED-CRYSTAL X-RAY SPECTROGRAPH—A DEVICE FOR THE ANALYSIS OF SMALL MINERAL SAMPLES[1]

I. ADLER AND J. M. AXELROD

ABSTRACT

A curved-crystal reflecting spectrometer of the type described by Birks and Brooks of the Naval Research Laboratories, but adapted for use in mineralogical studies, has been built in the Geological Survey. It has been successfully applied to the analysis of tiny crystals, zones in minerals, and individual grains in mixed-mineral specimens such as thin or polished sections, on grains or areas about 0.5 mm in diameter, X-ray diffraction spindles, and small samples of powder weighing a fraction of a milligram have also been analyzed without any loss or alteration of the sample. Of great value in thin- and polished-section work is the fact that this technique can be used to analyze selected areas without mutilating the specimen by digging out grains.

A modification of the curved-crystal spectrometer has made it possible to traverse a standard polished section in synchronization with a recorder, automatically plotting the distribution of various elements along a selected line. This method was applied, for example, to a polished section containing a central core of pyrite intergrown with and surrounded by a marcasite-like mineral. Chemical analysis of a concentrate of these two minerals gave selenium, cobalt, and iron as major constituents. A clear relationship between the cobalt, selenium, and iron was established by the X-ray method, identifying the second mineral as an intermediate member of the $FeSe_2$-$CoSe_2$ series.

INTRODUCTION

MINERALOGISTS, geochemists, and geologists are frequently faced with the problem of establishing the chemical composition of minute grains or minute inclusions in thin and polished sections. There is a particular need for a method of analysis that is rapid, nondestructive, and applicable to small samples, or, in the case of mounted composite specimens, small selected areas. One solution to such a problem has been the construction of a very fine microanalyzer by Castaing in France (5). This device, capable of analyzing sample areas of the order of one square micron, uses an electron beam as a probe and measures the emitted X-rays. The device is, however, best suited for metallic specimens and is very costly.

Birks and Brooks (4) have recently described a curved reflection-type focusing X-ray spectrometer and its application to the determination of microgram quantities of a number of elements. On samples weighing about 1 mg they have reported intensities, resolution, and line-to-background ratios that

[1] Publication authorized by the Director, U. S. Geological Survey.

are comparable to those obtained from a 10-gram sample on a commercial flat-crystal spectrometer. A modification of this instrument and details of construction are described in this paper.

To make clear the functioning of the curved-crystal X-ray spectrograph, the principles of fluorescent X-ray spectroscopy (*2*) are briefly reviewed. They are most readily understood by a comparison of the X-ray method with the optical emission method. Figure 1 shows the essential arrangement of both.

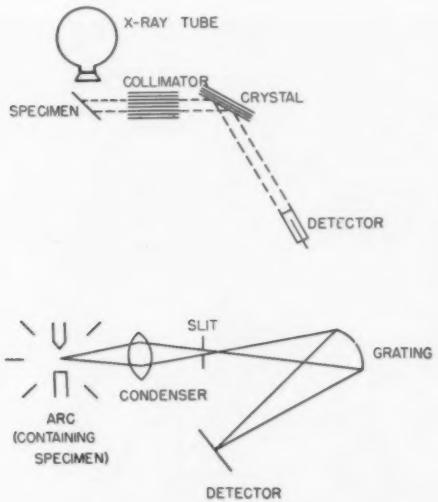


FIG. 1. Arrangement of (top) a flat-crystal X-ray spectrometer and (bottom) a curved-grating optical spectrograph.

In optical spectrography the ultraviolet and visible spectra are excited by means of an electric arc or high-voltage spark. The spectra are sorted into their component lines by means of a prism or grating and then recorded either photographically or electronically.

For fluorescent X-ray spectroscopy the exciting source is a high-energy X-ray tube. The continuous or white radiation falls on the specimen and causes it to radiate an X-ray spectrum that is characteristic of the elements in the sample. The spectral X-ray lines are sorted out by means of a grating (in this case a three-dimensional grating)—generally a large single crystal of lithium fluoride, rock salt, calcite, or quartz.

The early days of X-ray spectroscopy were filled with many spectacular successes: the discovery of new elements, the ordering of parts of the periodic chart, and definitive mineral research. H. G. J. Moseley was able to demonstrate that the number of elements from hydrogen to uranium, inclusive, was 92, and to show that there were still 6 missing elements. He was also able to establish that there were only 16 rare-earth elements between barium and

tantalum. The first investigation of a mineral by the X-ray technique was made by A. Hadding in 1922. This was followed in two years by the work of V. M. Goldschmidt and L. Thomassen who investigated the X-ray spectra of rare-earth elements extracted from or contained in a large number of different minerals. These developments were followed by the discovery of hafnium and the determination of halfnium in zirconium materials. There were many other discoveries, and it is surprising that this powerful tool failed to gain wide acceptance, particularly in the United States.

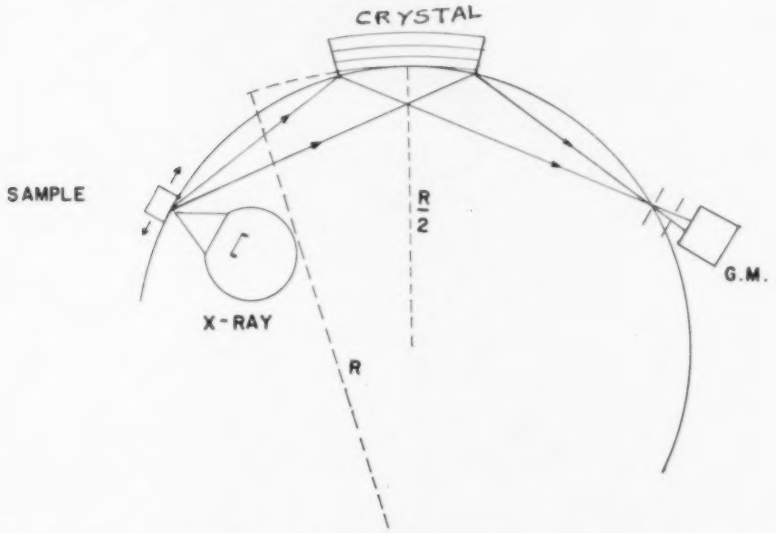


FIG. 2. Arrangement of a curved-crystal X-ray spectrometer, showing position of sample, X-ray tube, curved crystal, and Geiger-Mueller tube (G. M.).

The early workers had to face great experimental difficulties in building their own X-ray tubes and in working with relatively insensitive detectors. Today the application of these X-ray techniques has become comparatively simple. There are now commercially available X-ray sources and detectors that are astonishingly reliable and powerful.

THE REFLECTING CURVED-CRYSTAL X-RAY SPECTROGRAPH

The foundation for X-ray spectroscopy is the Bragg equation

$$n\lambda = 2d \sin \theta,$$

where n is the order of diffraction, λ is the wavelength, d is the distance between successive parallel planes in the crystal, and θ, the Bragg angle, is the angle of incidence of the X-rays upon the parallel planes. The modern flat-crystal spectrometer is so constructed that, as the crystal is rotated from a

position parallel to the collimated beam through 90 degrees, it will successively reflect all the wavelengths present in the fluorescence X-ray spectrum (up to $\lambda_{max} = 2d$) at the appropriate Bragg angle.

In the curved-crystal X-ray spectrometer, a curved crystal is used in a manner similar to the concave reflection grating of the optical spectrograph. Figure 2 shows the optical arrangement. The sample or sample slit, the crystal, and the detector slit lie on a focusing circle of radius $R/2$. The crystal plate, which is either rock salt or lithium fluoride, is bent plastically to a

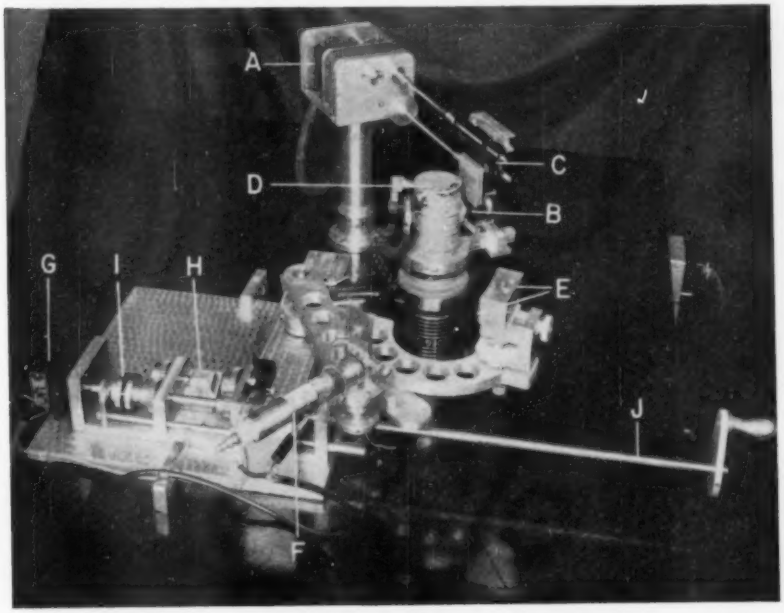


FIG. 3. Photograph of curved-crystal X-ray spectrometer. *A*, support and housing for small synchronous motor; *B*, polished section in position in instrument; *C*, mechanical stage of microscope; *D*, side-window X-ray tube; *E*, crystal-support block and bent crystal; *F*, halogen-filled Geiger-Mueller tube; *G*, small synchronous motor; *H*, Veeder-Root counter; *I*, clutch; *J*, crank for driving spectrometer by hand.

radius R and ground to a radius of $R/2$. A simple but effective method for accomplishing this has been described by Birks and Brooks (3). For a particular Bragg angle, θ, radiation of an appropriate wavelength, λ, is brought to a focus as indicated. As the crystal is moved along the focusing circle away from the sample or source, the spectrum of increasing wavelength is reflected from its surface in accordance with the relationship $L = (n\lambda/d)(R/2)$, where L is the distance to the center of the crystal surface, λ is the wavelength, d the crystal constant, and R the radius of curvature of bending of the crystal.

Because of the focusing optics a point or line source is used. This makes the instrument particularly valuable to the mineralogist.

Figure 3 shows the X-ray fluorescence spectrometer recently constructed at the U. S. Geological Survey. The protective housing has been removed to make various details visible. *A* is the support and housing for the small synchronous motor used for driving the specimen slowly across the X-ray beam. The specimen moves 1 mm per minute. The motor drives in synchronization with a strip-chart recorder. As will be described later this is useful for studying the distribution of an element in a polished section. A clutch arrangement makes it possible to disengage the motor drive and to manipulate the specimen by hand to position it correctly in the X-ray beam.

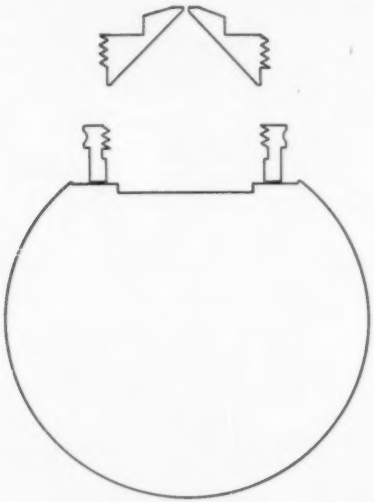


FIG. 4. Arrangement of X-ray tube, collar adapter, and pinhole collimator.

B is a polished section in position. The small area of the specimen being analyzed lies on the focusing circle. The specimens are the typical polished sections used for optical examination, which generally consist of minerals imbedded in plastic. The sample holder is made to take either 1¼-inch disks or 1-inch blocks, approximately half an inch thick. *C* is a microscope mechanical stage that permits easy and precise motion in two dimensions. *D* is a side-window (Machlett OEG-50) X-ray tube. The details of the beam collimator are described later. *E* is the crystal support block and bent crystal. It is mounted on a table that permits adjustment of the crystal position both for distance and tilt. *F* is a halogen-filled Geiger-Mueller tube. *G* is another small synchronous motor used to drive the spectrometer to trace out a spectrum, and it is run in synchronization with a strip-chart recorder. *H* is a Veeder-Root counter geared to read the 2θ angle directly. *I* is a clutch ar-

rangement for disengaging the motor drive so that the operator can drive the spectrometer by hand with the use of the crank *J*.

Figure 4 shows the collimating device for limiting the size of the X-ray beam. A collar adapter has been made to fit closely around the X-ray tube window. This collar adapter is threaded on the inside, and interchangeable pinhole collimators may be threaded into the collar. The pinholes vary in size from 1.0 mm to 0.25 mm. The collimators are made of lead and are cone shaped to get a pinhole image of the major part of the target. As the sample

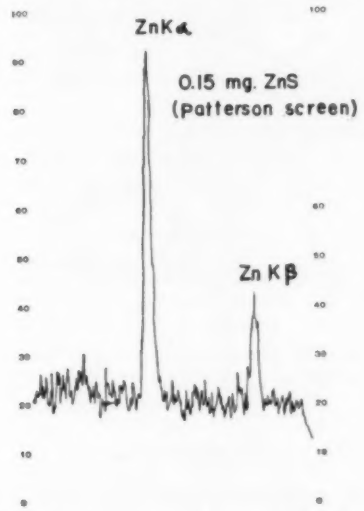


FIG. 5. Chart of zinc spectrum made from 0.15 mg of zinc sulfide.

is very close to the pinhole, there is very little divergence of the emitted beam and the spot remains small. In effect this is an X-ray beam probe that is useful for zoning studies.

APPLICATIONS

Analysis of Small Grains.—Specimens of extremely small size give excellent results. Figure 5 shows the strong signal obtained for zinc from 0.15 mg of zinc sulfide. In some cases it has been possible obtain positive results from grains almost invisible to the naked eye. Often it has been possible to analyze a single available grain, thus making it possible to identify the mineral.

Analysis of X-ray diffraction Spindles and Powder.—X-ray diffraction spindles and small samples of powders can be treated in the same fashion as small grains. Ambiguities in diffraction patterns can be resolved rapidly by determining the major elements present in the spindle. This is particularly

useful for isomorphous substances and members of solid-solution series. Here, as in the case of small grains, the X-ray spindle is recovered intact for future reference.

Polished and Thin Sections.—An example of the use of the curved-crystal spectrometer in the study of polished sections has already been reported (1). Sample areas as small as 0.5 mm in diameter can be analyzed. This technique has been successfully used for the determination of atomic ratios of selected elements such as arsenic-antimony ratios in tetrahedrite-tennantite.

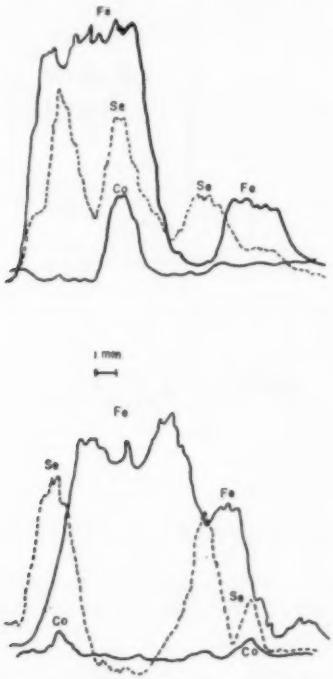


FIG. 6. Charts of the concentrations of iron, cobalt, and selenium along two lines across a polished section of pyrite with small grains of a second mineral intergrown along its edges.

Zoning Studies.—In the study of zoning one may either investigate selected areas for all detectable elements or one may mechanically traverse a polished section along a preselected path with the spectrometer set to detect a given element. These methods were recently applied to a polished section whose microscopic examination indicated pyrite with small grains of a second mineral intergrown along its edges. From optical considerations the second mineral might easily have been mistaken for marcasite. Chemical analysis had shown

selenium, iron, and cobalt. The specimen was traversed in three different areas with the spectrometer set alternately to detect iron, selenium, and cobalt in each area. It can be seen in the recordings (Fig. 6) that the selenium does not follow the iron but varies independently. It can also be seen that selenium will occur without cobalt, but the reverse is not true. Where a cobalt peak occurs, both selenium and iron are present. By examining these traces and relating them to the specimen it was possible to locate an isolated specimen of the small mineral grains. This was then positioned in the X-ray beam and found to contain major amounts of iron, selenium, and cobalt.

The results of this analysis indicated clearly that:

1. The pyrite was nonseleniferous.
2. The gangue contained areas showing native selenium or its oxidation products.
3. The small mineral grains were an iron-cobalt selenide, probably an intermediate member of the $FeSe_2$-$CoSe_2$ series. X-ray diffraction data had shown the members of this series to be isostructural.

LIMITATIONS

The present instrumentation is limited, because of air absorption of the soft X-rays and low fluorescence yield, to the detection of elements of atomic number greater than that of vanadium. By the use of a helium atmosphere, of crystals with a smaller radius of curvature resulting in a shorter optical path, and of greater *d*-spacing it should be possible to extend the method downward to many of the lighter elements.

ACKNOWLEDGMENTS

The authors wish to thank the following members of the Geological Survey: Joseph Abell and Camillo Massoni for their cooperation in the construction of the apparatus, and Robert Coleman and Charles Milton for mineralogical assistance.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
March 15, 1957

REFERENCES

1. Adler, I., and Axelrod, J. M., 1956, The curved-crystal X-ray spectrometer, a mineralogical tool: Am. Mineralogist, v. 41, p. 524–527.
2. Birks, L. S., Brooks, E. J., and Friedman, H., 1953, X-ray spectroscopy: Anal. Chemistry, v. 25, p. 692–697.
3. Birks, L. S., and Brooks, E. J., 1953, Uniform plastic bending of crystals for focusing X-ray radiation: Rev. Sci. Instruments, v. 24, p. 992.
4. Birks, L. S., and Brooks, E. J., 1955, Applications of curved-crystal X-ray spectrometers: Anal. Chemistry, v. 27, p. 437–440.
5. Castaing, R., 1954, Microanalysis by the electron-probe principle and corrections, *in* Nat. Bur. Standards Circ. 527, Electron Physics, p. 305–308.

THE ODARA PEGMATITE

C. V. PAULOSE

ABSTRACT

The paper is a study of the structural features of a complex zoned pegmatite in Central Travancore, S. India. The origin of the pegmatite is discussed in the light of the "replacement theory" and it is concluded that the theory cannot reasonably be applied in this case.

INTRODUCTION

PEGMATITES containing rare minerals have been and is a subject of much interest both from the economic and the scientific points of view. Some radical deviations from the old conceptions regarding the origin of pegmatites has been suggested as a result of recent investigations. Their application in the present case is dealt with at a later stage.

Location.—The pegmatite under study is located at a place called Odara (Lat. 9°22′ N and long. 76°38′ E) in the Thiruvalla taluk in Central Travancore. From Figure 1, it will be seen that the spot is within 6 miles by road from the two important towns of Central Travancore, viz., Thiruvalla and Chengannoor. Through these towns pass the Main Central Road. The water route is by canal which connects the area with the Manimalai river, a tributary of the Pamba river. Pamba river in turn is connected with the backwater navigation routes of Travancore and Cochin.

Previous Work.—A note on the occurrence of radio-active Columbite in the Odara pegmatite (5) is the only available published literature on this subject.

STRUCTURAL FEATURES

The pegmatite occurs as a straight dike cutting through the lateritized gneiss (country-rock) in a N–S direction and making an angle of nearly 30° with the ground surface. The overall thickness of the dike varies between 18 ft. to 26 ft. and the thickness of the inner quartz core between 12 ft. to 18 ft. Mining operations have removed a good length of the pegmatite.

Zoning in the Pegmatite.—The dike shows all the qualities of an ideally zoned pegmatite. The innermost quartz core is surrounded by an intermediate, typically pegmatitic zone containing most of the rare minerals. This second zone is again surrounded by the outermost zone which is in contact with the country rock.

Mineralogy of the Zones.—The following general features are noted:

(1) The inner core consists of massive, translucent, slightly milky quartz and embedded in it are crystals of aquamarine of varying sizes which are visible only upon breaking of the quartz. In several of the quartz lumps, crys-

tals of aquamarine radiate in different directions from common points. This zone contains the major portion of the aquamarine crystals found in the pegmatite. It is the only variety of beryl present in this zone.

(2) The intermediate zone contains all the varieties of minerals found in this pegmatite; viz., quartz, feldspar, small beryl crystals of different hue, columbite, muscovite, and magnetite. The massive lumps of feldspar are kaolinitized. Small beryl crystals are embedded in or protrude out of the partly decomposed feldspar lumps. The quantity of beryl available in this zone is quite insignificant in comparison with what is found in the inner core. Columbite in very small quantity and in partly developed crystals is formed

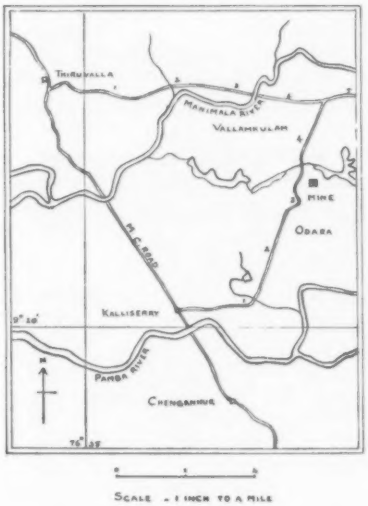


FIG. 1. Index map.

at the junction between the quartz core and the intermediate zone. The mineral shows association with both quartz and feldspar. It also occurs as thin plates in between mica flakes which in turn are embedded in small quartz lumps.

(3) The outer zone of the contact zone, contains disintegrated quartz fragments, completely decomposed clayey feldspar, a good quantity of small books of muscovite, and a few lumps of magnetite. None of the other minerals are seen in this zone.

The structure of the pegmatite may be diagrammatically represented as shown in Figure 2.

DESCRIPTION OF MINERALS

Beryl.—Four varieties of this mineral are seen in the pegmatite. Beautiful sea-blue aquamarine is the important variety with smaller quantities of bluish-white common beryl, yellow beryl, and greenish beryl. Aquamarine crystals range from 1 in. to 2 ft. in length and 0.5 to 4 in. in diameter. Perfectly developed prismatic and flat basal faces and a slight tapering towards one end are the prominent features of these crystals. Slight bending of a few of the crystals is also noteworthy. The transparency of the crystals is marred by internal cracks. Aquamarine and yellow beryl crystals show patches of transparent portions in between the cracks. These transparent pieces possibly can be cut into gems.

Optical Properties.

(1) Aquamarine—Sea blue in color; cleavage—0001 poor; non-pleochroic in thin sections and slightly pleochroic in thick fragments with X = faint blue, Z = colorless; refractive index [1] e = 1.584, w = 1.591; w-e = .007; uniaxial and negative.

(2) *Yellow beryl.* Faint golden-yellow in color; cleavage—0001 poor; non-pleochroic in thin sections and slightly pleochroic in thick fragments with X = very faint yellow, Z = colorless; refractive index e = 1.572, w = 1.577; w-e = .005; uniaxial and negative.

Chemical Properties.

Constituents	Aquamarine	Yellow beryl
SiO_2	65.17	65.59
Al_2O_3	18.46	18.73
Fe_2O_3	1.73	0.61
FeO	0.41	1.53
BeO	12.53	11.94
CaO	0.07	0.05
Na_2O	0.23	0.07
K_2O	..	0.03
P_2O_5	0.04	0.05
H_2O^+	1.55	1.34
H_2O^-	0.02	0.04
Total	100.21	99.98
Sp. gravity	2.713	2.722

Analyst: C. V. Paulose.

The figures given above represent only the optical properties and chemical compositions of two crystals of beryl, belonging to the two varieties that were available for this study.

Columbite.—Physical and Optical Properties.—Cleavage—fairly distinct in one direction; fracture—uneven; brittle; hardness—6; sp. gravity—5.57; lustre—submetallic; streak—black; radio-activity—U_3O_8 equivalent of 0.25 percent; opaque in thin sections.

[1] Refractive indices determined using Leitz jelley refractometer.

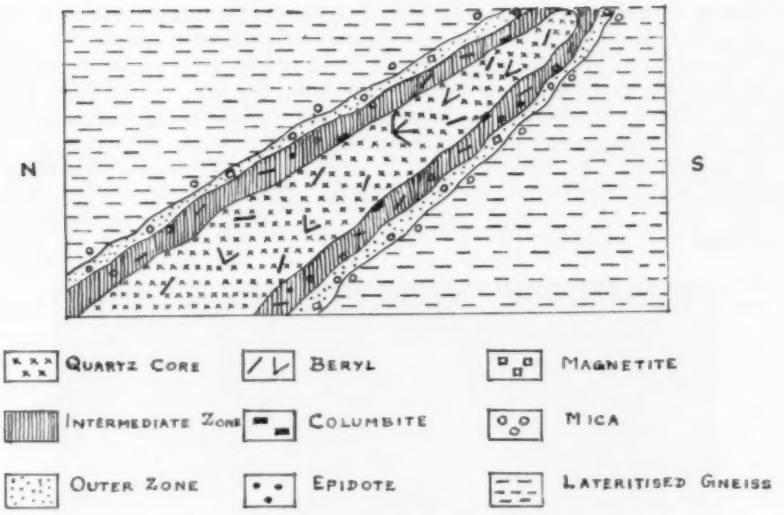


FIG. 2. Sketch Section of Odara Pegmatite.

Chemical Properties.

Constituents	Columbite
Nb_2O_5	62.21
Ta_2O_5	9.83
SiO_2	tr.
Fe_2O	3.57
FeO	13.50
MnO	10.77
U_3O_8	0.29
H_2O^+	0.00
H_2O^-	0.02
Total	100.18

Analyst: C. V. Paulose.

The percentages of niobirum and tantalum oxides obtained in the above chemical analysis of a crystal of the mineral used in this study agree very well with the theoretical quantities that could be determined from the graph prepared by Jahns (3), based on several published analyses of the mineral.

Muscovite.—This is the only variety of mica available in the pegmatite. Thin sheets are transparent. Books of mica found in the outer zone exhibit a dark tint towards the centre of the cleavage plates. This coloration appears to be due to hematite inclusions. Many of the books are marred by 'A' reaves and cracks. Some show leaf structure with the characteristic mid-rib (Fig. 3).

Feldspar.—Feldspar in the pegmatite is in a state of alteration into clay. Apparently fresh lumps of the mineral, particularly in the intermediate zone, exhibit perthitic characteristics. Under the microscope this perthite shows

signs of sericitization. Chemical tests indicate a high potash content of the mineral. Feldspar in the outer zone is completely altered into clay.

Quartz.—Slightly translucent quartz is the predominant variety, however. Some of the lumps here and there exhibit a smokey hue. In addition to a 2½ ft. diameter crystal of pale pink quartz, a few partly transparent tapering crystals of smoky quartz protrude from the central core of massive quartz.

Magnetite.—The mineral occurs as small lumps of irregular shape dispersed in the intermediate and outer zones. The magnetite seems to have been derived from the main igneous body and carried up by the magma as suggested by Lindgren (4).

FIG. 3. Mica showing leaf structure.

ORIGIN OF THE PEGMATITE

A description of a single pegmatite with definite features probably does not warrant any elaborate discussion and generalization on the origin of pegmatites. Hence, only the following two important views and their application relating to the origin of pegmatites are considered here.

(1) The composition of the pegmatite represents the extreme acidic facies of molten magmas charged with gaseous matter and metallic vapors. The vapors are responsible for the zoning and the rare mineral content of these rocks.

(2) The pegmatite was formed in two phases: (a) consolidation of an original quartz-orthoclase magma as graphic granite. (b) Successive replacement of the original minerals by a series of hydrothermal solutions. Well-

known as the "replacement theory," this theory claims that zoning and formation of rare minerals take place during the second phase of development of a pegmatite.

ODARA PEGMATITE AND THE "REPLACEMENT THEORY"

Field evidences relating to the Odara pegmatite do not give any clues which indicate that the rare mineral assembly of this zoned dike is the result of replacement. On the other hand, the following evidences weigh in favor of attributing a single phase consolidation of the magma with the zoning being effected by other causes.

(1) In the outermost zone, mica is present in greater quantity as compared to other zones. This seems to indicate that the initial hot magmatic solution, highly charged with steam and light metallic vapors, penetrated the country-rock and on being chilled deposited the mica in the contact zone. The presence of mica deep within the country-rock at the points of contact adds strength to this supposition. In this process, the hot solution might have been aided by the alumina and the water content of the country-rock.

(2) The assemblage of minerals in the intermediate zone indicates the natural effects of crystallization in a pegmatite magma that was most likely charged with heavier metallic vapors and mineralizing solutions that followed the lighter portions that contributed to the formation of the outer zone.

(3) The central quartz core represents, quite likely, the residual quartz which is usually the last mineral to crystallize in any magma. The presence of the major portion of the beryl crystals embedded within this quartz core indicates that the constituents that contributed to the formation of the mineral were present in the magma at the time of the outflow.

(4) Tapering of beryl crystals both in the central and intermediate zones is also significant. It may indicate the effect of slow movement of the magmatic fluid at the time of crystallization of the mineral.

(5) The bending seen in a few of the beryl crystals of the central core suggests that the crystals remained plastic for some time due to the heat of the magma and also that the magma was subject to minor local disturbances.

(6) The sericitization in the perthite seems to have been effected by percolating solutions from the lateritized country-rock rather than by any subsequent outflow of hot mineral solutions.

The above evidences make the author feel that the "replacement theory" need not always be applicable to the development of zoned, complex pegmatites. Cameron and colleagues (2) after their investigation on the New England mica deposits remark: "In most of the pegmatites, field studies, however, have given no indication that the zones themselves were developed by hydrothermal replacements of pre-existing massive pegmatite." Almeida and colleagues (1) in their contribution on the pegmatites of Northern Brazil give expression to a similar view. They say "we have no evidence from the field relations of these dikes to suppose that the present mineral assembly is the result of a series of replacements as has been suggested by Schaller and others."

ACKNOWLEDGMENTS

The author's grateful thanks are due to Dr. C. S. Pichamuthu, former Director of Geology in Mysore for extending to him laboratory facilities in the Mysore Geological Department, Bangalore, and for all the encouragement given during the course of the work. He also proffers his thanks to the University of Travancore for the award of a Special Research Scholarship.

CENTRAL RESEARCH INSTITUTE,
UNIVERSITY OF TRAVANCORE,
TRIVANDRUM, S. INDIA,
April 1, 1957

REFERENCES

1. Almeida and others, 1944, The beryl-tantalite-cassiterite pegmatite of Paraiba and Rio Grande Do Norte, North-eastern Brazil: ECON. GEOL., v. 39, no. 3.
2. Cameron, E. N., and others, 1945, Extracts from structural and economic characteristics of New England mica deposits: ECON. GEOL., v. 40, no. 6.
3. Jahns, R. H., 1951, Geology, mining and uses of strategic pegmatites: Min. Eng., p. 45–59.
4. Lindgren, W., 1933, Mineral Deposits, p. 753.
5. Paulose, C. V., 1950, Occurrence of radio-active Columbite in Travancore: Curr. Science, v. 19, p. 277–278.

SCIENTIFIC COMMUNICATIONS

A SUGGESTED INTERPRETATION OF THE QUEBEC–LABRADOR IRON DEPOSITS

G. VIBERT DOUGLAS AND L. P. COMPTON

ABSTRACT

A new interpretation for the sequence of events in the Knob Lake area is given. It is suggested that they are more closely allied to the Wabana type than the Mesabi.

There are apparently few papers dealing with the interpretation and genesis of these important iron deposits. Retty and Moss (5) believe that the ores are the result of the leaching of the iron formation by meteoric waters. Harrison (2) supported this hypothesis.

The geological succession as given in the Iron Ore Company of Canada's table, which was distributed with the typical specimens to the universities, seems to open the way to a new interpretation.

The table as given, is as follows:

	Point Series	Menihek formation—shales and dolomite (150–1,000′)
		Unconformity
		Sokoman formation—ferruginous beds (150–600′)
	Ferriman Series	Ruth formation—ferruginous slates (10–100′)
		Wishart formation—quartzite (80–160′)
Pre-cambrian		Unconformity (?)
		Fleming formation—chert breccia (0–300′)
	Hamilton Series	Denault formation—dolomite (0–600′)
		Attikamagen formation—gray and green shales (0–1,200′)
		Seward formation—quartzites and grits
		Unconformity
		Ashuanipi Complex

The present authors believe that the Hamilton Series is a ternary succession on a sinking floor. The land mass lay to the west and the shallow seas to the east. This sequence is quite a normal one, with the exception of the Fleming Chert breccia. It is suggested here that this rock is a surface breccia, which would imply elevation of the area so that the Denault dolomite was exposed to sub-aerial erosion. Siliceous, meteoric waters brought about the solidification of the breccia (6).

The base of the Ferriman Series is the Wishart quartzite which may be considered as a basal bed, and the start of a new cycle of events. The order of the rocks supports the idea of a very shallow sea or inlet with a succession of interrupted events. The present writers consider that the ore was laid down in somewhat the same manner as that invoked by A. O. Hayes (3) in his classic paper on Wabana. At Wabana a number of beds of hematite were deposited in a marine environment. Oolitic texture is common in both the ores of Wabana and Knob Lake.

At Knob Lake, in the Sokoman formation the various beds are now grouped according to A. M. Crooks (personal correspondence) as follows:

— Top —

Upper Iron Formation
- Lean Cherty—gray in color, some blue hematite
- Slate
- Red Cherty—blue hematite and red chert
- Yellow—high carbonate content
- Gray—lean, gray in color, blue hematite

Middle Iron Formation
- Red Cherty—blue hematite and red chert
- Yellow-Brown—high carbonate content
- Gray and Pink—gray, white, pink and red oolitic chert, with disseminated hematite and bands of hematite

Lower Iron Formation
- Red Cherty—oolitic blue hematite with dark red chert and bands of hematite and chert
- Yellow Cherty—(S.O.I.F.), silicates and carbonates with limenite, some manganese

---

Ruth Slate forming floor.

This sequence of red, yellow, gray, which is thrice repeated, would indicate three periods of iron deposition on a mud floor. There must have been a hyatus between the three depositions with the water table of the area standing at the level that is now represented by the change from yellow to red. If the iron had been originally deposited as iron hydroxide $Fe(OH)_2$ and then gradually dehydrated to limonite and hematite, the line of demarkation would be the water table of the area with the hematite above and the limonite below.

The next event was the burial of these deposits by muds that have formed the slates and given the grayish appearance to the cherty member, and sealed off the previous and foregoing events, thus preventing further oxidation. This whole sequence was then repeated in the Upper Iron formation. At Wabana at least six distinct beds are known. These have been gently tilted and sub-

jected to minor faulting. At Knob Lake on the other hand, there has been severe folding and faulting.

In conclusion the writers believe that the deposits at Knob Lake are more akin to the Wabana type, than to the generally accepted sequence of events which have produced the Mesabi deposits.

ACKNOWLEDGMENTS

The writers wish to thank Dr. Moss, Dr. Dufresne, Mr. Neal, and Miss A. M. Crooks for discussion and information. They are in no way responsible for the views given.

DALHOUSIE UNIVERSITY,
HALIFAX, NOVA SCOTIA,
April 30, 1951

BIBLIOGRAPHY

1. Crooks, A., 1957, Personal Correspondence.
2. Harrison, J. M., 1952, The Quebec-Labrador Iron Belt, Quebec and Newfoundland: Geol. Surv., Canada, Paper 52–20.
3. Hayes, A. O., 1915, Wabana Iron Ore of Newfoundland: Geol. Surv., Canada, Mem. 18.
4. Moss, A. E., 1957, Personal Correspondence.
5. Retty, J. A., and Moss, A. E., 1951, Abstract to Iron Ore Deposits of New Quebec and Labrador: ECON. GEOL., v. 46, p. 799–800.
6. Twenhofel, W. H., 1950, Principles of Sedimentation: New York, McGraw-Hill Book Co., Inc.

DISCUSSIONS

GEOTECTONICS AND URANIUM MINERALIZATION, AUSTRALIA

Sir: D. W. Bishopp, ECON. GEOL., No. 1, 1957, has criticised the methods of expression in J. Rade's paper "Notes on the Geotectonics and Uranium Mineralization in the Northern Part of the Northern Territory, Australia" (ECON. GEOL., no. 4, 1956) on the grounds of "Geologese." Unfortunately the subject matter of Mr. Rade's contribution is even more open to criticism.

Over the past 4 years the whole of the Katherine-Darwin area has been mapped on a scale of 1 inch to the mile by geologists of the Bureau of Mineral Resources, Geology and Geophysics. This mapping does not confirm any of Mr. Rade's theories on the tectonics of the region; his summary of the stratigraphy is neither up-to-date nor accurate.

It is difficult to understand precisely what Mr. Rade is driving at and even more difficult to reconcile his postulates with the known geology of the region. Mr. Rade appears to have based an imposing theory on a study of four structures, three of which are minor, local shears. On this inadequate basis he has invoked Kraus, Bubnoff and others in order to relate these structures to theoretical events of regional importance.

On the structure map accompanying the paper four structures are shown. One of these, the Giant's Reef Fault at Rum Jungle is of regional importance. The remaining three are insignificant strike shears that localize minor uranium occurrences, or, as in the case of the shear located near Burrundie—only negligible anomalous radioactivity. The Burrundie shear has a strike length of probably 200–300 feet; the Brocks Creek shear probably less. There is no justification for assigning regional importance to individual structures of this size.

Mr. Rade's hypothesis of a couple caused by the differential movement of the Cullen Granite is staggering. There is no evidence to suggest movement of the Cullen Granite mass, which is a normal, discordant, pluton intruded at a fairly high level and surrounded by a hornfels aureole. Further, the Cullen Granite is cut by the same system of fractures that Mr. Rade claims to be a result of the "couple." This would appear to be a case of the effect being impressed very markedly on the cause.

In addition to postulating differential movement of the granite, Mr. Rade introduces a "curving of the orogen," which is not substantiated by regional geological mapping.

The paper clearly demonstrates that the author's knowledge of the geology of this part of Australia is not adequate to justify his excursion into the "realm of cloudy hypothesis" to which Mr. Bishopp so aptly refers.

B. P. WALPOLE

CANBERRA, AUSTRALIA,
May 6, 1957

PITCHBLENDE-BEARING VEINS, CENTRAL CITY DISTRICT, COLORADO

Sir: In connection with the article, Paragenesis and Structure of Pitchblende-bearing Veins, Central City District, Colorado, by P. K. Sims (THIS JOURNAL, Vol. 51, p. 739–756) I conducted a geochemical soil survey in 1955 on the Black Hawk Lode No. 1 claim on Silver Hill in the peripheral zone and found the following:

Over the Northwest-trending fractures, copper vallies ranged from 300–1,000 p.p.m. with zinc vallies from 0–50 p.p.m. Over the sphalerite-metatorbenite Northeast-trending fractures, copper vallies ranged from 0–50 p.p.m. with zinc vallies from 500–2,000 p.p.m. The Northeast set of fractures was extended about 500 feet with about one-foot soil overburden.

JOHN S. VANDERPOOL

INSPIRATION CONS. COPPER CO.,
CHRISTMAS, ARIZONA,
April 26, 1957

SULFUR ISOTOPES: A REPLY TO PROFESSOR McKINSTRY [1]

Sir: We are grateful for Professor McKinstry's comments (this Journal, p. 196–198) concerning our paper (Vol. 51, 139–149) on the relative abundances of the isotopes of sulfur in sulfide minerals. He has pointed out several factors in the use and misuse of such data as we presented which we had failed to emphasize. We do feel, however, that he has somewhat misunderstood the intentions of the paper.

The thesis of our paper was that the ratio of the isotopes of sulfur in a sulfide sample might be useful in determining the ultimate origin of the ore-forming solutions. It is assumed, as pointed out by Professor McKinstry, that the sulfur contained in the mantle of the Earth has a uniform isotopic composition equal to that of meteoritic sulfur. As he states, these assumptions rest on "grounds of logic rather than on direct evidence." The reason for this is, of course, that no direct evidence is available. In such a situation it would seem that assumptions based upon logically derived conclusions from available astronomic, geologic, and geochemical data are the best obtainable, and their use is wholly justified. They are, naturally, subject to error, but then so is "direct evidence."

We have then assumed that primary sulfides reaching the oxidation zone at the Earth's surface have undergone partial or complete oxidation to sulfate.

[1] Lamont Geological Observatory Contribution No. 252.

Most of this sulfate was then taken into solution by sea water and much was reprecipitated as sulfates in evaporate sediments or reduced by bacterial action and incorporated as sulfides in shales and other detrital sediments. These assumptions seem safe enough, being based on general geologic considerations. Since oxidation-reduction reactions undergone by sulfur compounds are known by both theory and experiment to produce large fractionation of the isotopes of sulfur with the heavier isotope concentrating in the oxidized form, we have assumed that sulfur incorporated in a sedimentary facies dominant in sulfate would be enriched in the isotope Sulfur-34, while sulfur incorporated in predominantly argillaceous sediments, and more likely consisting of sulfides, would be enriched in Sulfur-32. The applicability of this assumption to any particular area may certainly be questioned on the basis of the geology of the underlying rocks, where this geology is thoroughly known. However, the general principle that some masses of sediment will have a higher and some a lower Sulfur-32 to Sulfur-34 ratio than does the sulfur within the Earth's mantle seems to be valid. Therefore, when a mass of sediment is subjected to orogenic forces or magma formation subsequent to its deposition, and all or part of its sulfur content is incorporated into hydrothermal solutions, the isotopic composition of the sulfur carried by these solutions will reflect the history of the segment of the Earth's crust from which they were derived.

In trying to apply this hypothesis to studies of ore deposits all of the geologic relations of the deposit must be considered. The isotopic data represent an important but not sufficient line of evidence applicable to the deciphering of the geology. Isotopic analyses are no more foreign to geologic investigations than are chemical analyses, X-ray studies, petrographic studies, or analyses of rock structure and paleontology. Each of these types of study requires special equipment and techniques, and each is best done by an expert in that field. However, all have a place in geologic research.

Perhaps our applications of the isotopic data to the problem of the origin of the ore bodies in Central New Mexico, in the Mississippi Valley, and at Ivigtut are in error. If so, however, this must be shown on the basis of the geology of these areas, not on philosophy. To the best of our knowledge and ability we have based our interpretations upon the geologic relations at the deposits discussed.

We agree that it is "too early in the new game to rule out all modes of fractionation other than sedimentary." We hope to do more work on this problem ourselves and we are sure that others will engage in similar research. However, all of our past attempts to find fractionation effects produced by liquid-gas interactions or other plausible fractionation producing mechanisms have failed. Since we know that oxidation-reduction reactions do produce fractionation we have attempted to synthesize explanations of the available isotopic data on the basis of such reactions. We feel that this is preferable to using reactions completely unjustified by experimental data.

We also agree that careful sampling is necessary if analyses of the samples are to be most meaningful. However, as we are sure Professor McKinstry realizes, careful sampling is costly. In our preliminary work we felt that easily obtained museum specimens offered the most useful and, at the same

time, most inexpensive source of samples. Until we knew what sort of results we could expect we naturally did not know which areas would merit careful sampling and on which areas it would be wasted. In our subsequent investigations, which we hope will be published shortly, we have devoted much effort to obtaining fully described samples.

Finally we wish to concur that "geologists need not be overawed by the mysteries of a new technique to the extent of accepting its first implications as infallible gospel." However, we would further urge the geologist to accept neither the later results of these techniques nor the past or future results of any technique as "infallible gospel." The geologist, if he is to consider himself a scientist, must continually question all the assumptions and conclusions of geologic research. No premise of geology, even the most revered, should be held to be above questioning.

HERBERT W. FEELY,
J. LAURENCE KULP,
WAYNE U. AULT

LAMONT GEOLOGICAL OBSERVATORY,
COLUMBIA UNIVERSITY,
PALISADES, N. Y.,
June 13, 1957

HEAT AND TEMPERATURE IN ORE DEPOSITION

Sir: I was impressed with a treatise on ore deposition by Dr. C. J. Sullivan in your ECONOMIC GEOLOGY, v. 52, No. 1, Jan.-Feb. 1957, p. 5–24. The author advocates, if I understand correctly, that heat and temperature are the dominant factors in ore-forming process and the hydrothermal solution theory may be disregarded, or at least considered as of secondary importance. In one of the applications of his theory the author referred to a typical zonal arrangement of metallic sulfide minerals that is directly related to thermal stability range and corresponding hardness of each mineral.

In many hydrothermal sulfide deposits that exhibit zonal arrangement of the "ore minerals" the representative or dominant gangue minerals may be found also in zonal arrangement, in descending order, quartz, chlorite, and calcite, as shown below:

	Sulfide ore minerals	H	Representative or dominant gangue minerals	H
Temperature increase	Galena	2.5–2.75	Quartz	7.0
	Sphalerite	3.5–4.0	Chlorite	2.0–2.5
	Chalcopyrite	3.5–4.0	Calcite	3.0
	Pyrite	6.0–6.5		

It appears that gangue minerals that ascended with the sulfides from the same source are not in harmony with the sulfides, but exactly reverse in zonal arrangement, when calculated by hardness and thermal stability.

Doesn't this suggest that the chemical nature of ore-forming fluids has something to do with the process of ore deposition?

The result of my experiment on secondary sulfide enrichment (ECON. GEOL., v. 9, No. 8, Dec. 1914, p. 745) shows relative stability of sulfides and gangues in N/8 sulfuric acid, and in increasing orders they are calcite, rhodochrosite, siderite, nephelite, pyrrhotite, leucite, tetrahedrite, labradorite, hornblende, galena, augite, sphalerite, biotite, fluorite, orthoclase, chalcopyrite, arsenopyrite, marcasite, muscovite, pyrite, and quartz. Though the experiment was carried out at room temperature and in cold acid solution, yet it may be inferred that similar results would be recorded at boiling temperatures. This experiment in 1914 incidentally suggests 1) possible acidic nature of the ore-forming fluid, as Graton ascertained (ECON. GEOL., v. 35, Supp. No. 2, Mch.-Apr. 1940); 2) zonal arrangement of sulfide minerals, as theorized by Emmons (Trans. A. I. M. E., v. 70, 1924, p. 964–997); and 3) common association of hydrothermally altered minerals; altogether would be regarded as rather convincing evidences of possible acidic nature of mineralizing ascending solutions.

In connection with the subject questions may be raised to explain why ore-forming fluid is of alkaline nature in "depth," as suggested by Graton (ECON. GEOL. v. 35, Supp. No. 2, Mch.-Apr. 1940); why sulfide ore bodies pinch out in depth; why hydrothermal alteration of the wall rock decreases in depth and finally disappears; why igneous host rock becomes fresh in depth in harmony with the pinching out of vein and fissures; why primary gangue minerals are basic in depth and acidic in upper horizon; why native copper incrusted with malachite and azurite occur in peridotite or serpentine or calciferous rock; why chalcocite (with bornite) incrusted with malachite and azurite with absolute absence of pyrite or marcasite occur in calciferous rock or porphyritic andesite or vesicular andesite lava with zeolites; what was then the chemical nature of hot ore magma before differentiation; what was the chemical nature of the remaining ore magma after each stage of mineral differentiation; at what stage the "ore fluid" becomes alkaline and then acidic; what are the mineral constituents of the solution at each different stage or zone of deposition with respect to the chemical nature of the solution and thermal stability?

Precise field observations and logical enquiry into the chemical nature of "ore-forming fluid" shall, I believe, lead to an acceptable solution of these unknowns and bring us to the final understanding of the "secret" of ore deposition.

HIRONAO NISHIHARA

91 KOMAGOME ASAKACHO,
BUNKYO-KU, TOKYO, JAPAN,
April 30, 1957

IS LEUCOXENE ALWAYS FINELY CRYSTALLINE RUTILE?—A REPLY

Sir: In the December, 1956, number of this journal (1), an article by the writers and others (2) is discussed by V. T. Allen, and several questions are asked concerning the nature of leucoxene. Professor Allen summarizes his

own experience with leucoxene and concludes that it may be crystalline rutile, sphene, anatase, or brookite, or an amorphous material.

In view of the many data on the composition of leucoxene published by numerous investigators, the question asked in Dr. Allen's title seems hardly necessary, since the answer must obviously be in the negative. Our own investigation confirmed this to the extent that one of the four leucoxene grains X-rayed proved to be brookite. Being aware of the composition diversity of leucoxene, we were at some pains to confine our conclusions to the beach sands we studied. At this stage of investigation of beach sands, no generalizations applicable to all beach sands are justified.

We have recently investigated in detail a large number of individual leucoxene grains. Table 1 contains the results of an X-ray study of 100 leucoxene grains taken at random from fraction no. 2 of a Mozambique beach sand we described in the original article (2, Table III, p. 275). The results are of interest because they show that although rutile is the predominant constituent, anatase is also present along with rutile in 1 out of every 5 grains. Brookite is a minor constituent. Dr. J. A. Hartman, formerly of this Department, has studied the leucoxene present in bauxites and associated clays from six different localities. His results (4) further confirm the variability of leucoxene and also suggest that environmental factors determine whether one TiO_2 polymorph or another will be predominant in the alteration products. X-ray diffraction photographs of nearly 200 individual leucoxene grains show that both rutile and anatase are present.

The chief difference between Professor Allen and ourselves is in the usage of the term leucoxene. He recommends "that leucoxene should be retained as a petrographic term for the alteration product in which titania occurs in rocks." In keeping with the fact that leucoxene as he describes it is not one but a group of products of alteration, his statement should be modified to read "a petrographic term for *any* alteration product in which titania occurs in rocks." From the viewpoint of the petrographer, this is a convenient usage, for in thin section it is often not possible to go beyond recognizing that a fine-grained aggregate has formed by alteration of some titanium-bearing mineral. We do not object to such usage in petrography nor to the inclusion of amorphous alteration products under leucoxene, as suggested by Allen. The use of a group term of this type when differentiation of the individual components is difficult or impossible is well implanted in the geologic literature; e.g., limonite, wad, bauxite, allophane, etc. If differentiation is possible, however, then more specific terms should be used. In studies of titanium minerals in polished surface in reflected polarized light, it is frequently possible to distinguish several different alteration products of titanium minerals, and the use of the term leucoxene to cover them all is not satisfying. In the study of beach sands, the use of leucoxene to include both amorphous iron-titanium oxides and finely crystalline TiO_2 is particularly unsatisfactory, for practical reasons. Amorphous iron-titanium oxide has essentially the same iron oxide content as unaltered ilmenite, whereas finely crystalline TiO_2, for which we reserved the term leucoxene, carries 75 to 92 percent TiO_2, and concentrates containing sizable amounts of such material are the high-grade "ilmenite" of commerce.

For this reason, in describing beach sands and discussing the alteration of ilmenite, we preferred to follow Tyler and Marsden (5), who restricted the term leucoxene to finely crystalline TiO_2. It is interesting to note that Cannon (3), in discussing the alteration of ilmenite at Trail Ridge, followed the same usage as we did. In this connection, our summary (2, p. 264) of Cannon's work is so clearly referred to Trail Ridge that we find it difficult to believe that the reader will be misled by our citation of Cannon's statement on lines 15 and 16 of page 210 of his article.

Dr. Allen's second question is: Has the amorphous iron-titanium oxide of Stage 2 a higher moisture or water content than that of leucoxene of Stage 3? We cannot answer this. Water was not determined in the samples studied.

TABLE 1

X-RAY IDENTIFICATIONS OF 100 LEUCOXENE GRAINS

A. Summary of results

Composition	Number of leucoxene grains
Rutile (oriented)*	68
Rutile (random)*	7
Brookite (random)	1
Rutile-anatase mixtures	20
Rutile-brookite mixtures	4
Total	100

B. Description of mixtures (first-named component is the dominant one)

Mixture	Number of grains
Rutile (oriented)* + anatase (oriented)	9
Rutile (oriented) + anatase (random)	5
Rutile (random) + anatase (random)	1
Anatase (oriented) + rutile (oriented)	5
Rutile (oriented) + brookite (oriented)	2
Brookite (oriented) + rutile (oriented)	2
Total	24

* "Oriented" means that the grain is an aggregate of crystals in parallel orientation; "random" means that the grain is composed of crystals randomly oriented.

The matter of water content is one of several problems of the chemistry of alteration involved. Beach sands, however, because of their fine grain size and because of the impossibility of obtaining fractions consisting solely or even largely of one alteration product, are not ideal for chemical studies.

Dr. Allen's third question is: Is it possible to decide whether the X-ray patterns of the leucoxene in beach sands represent the bulk of the leucoxene present or a few well-crystallized spots or grains? This is readily answered for our beach sand samples. In polished surfaces, the increasing crystallinity as alteration proceeds from amorphous iron-titanium oxide to leucoxene is obvious. Furthermore, the completeness of the X-ray patterns and the intensities of the lines and spots contained are comparable to those to be expected from completely crystalline samples. As a further check on crystallinity, X-rayed leucoxene grains of each category shown in Table 1 above were examined individually in transmitted light. This inspection confirmed ob-

servations in reflected light. The grains are aggregates of minute crystals. Amorphous material, if present, must be in trace amounts. It will be noted in Table 1 that oriented aggregates of crystals are more common than random-oriented aggregates. This was also confirmed by examination in transmitted light.

Dr. Allen has cited from his own experience several cases in which leucoxene has been shown to be amorphous by X-ray study or in which X-ray patterns have been obtained from samples believed to contain only 1 to 2 percent of crystalline material. This provoked his question as to how much of a well crystallized mineral such as rutile, anatase, sphene, or brookite need be present to give sharp lines in its X-ray pattern. This question should be answerable in principle.

In mixtures of a crystalline TiO_2 polymorph with amorphous material of essentially the same composition the intensities of the X-ray patterns should vary in a linear fashion with the amount of the crystalline phase present, since the absorption coefficients of the crystalline and amorphous components would be similar. If only a very small amount of the crystalline phase is present, only the strongest lines of its X-ray pattern will be visible on a photograph of normal exposure. A progressive increase in the proportion of the crystalline phase present relative to the amorphous material will cause a progressive increase in the intensity of the strongest lines and the appearance on the photograph of those less intense lines of the pattern which previously were not visible. For standard sample sizes, exposures, and processing conditions, even a rough examination of the number of lines present on an X-ray photograph, along with their intensities, will tell whether a sample is predominantly crystalline or amorphous. More quantitative results can be obtained by comparing the intensity of a selected line from the pattern of the crystalline phase with that of a line from an added internal standard or with the intensity of the primary X-ray beam. The foregoing technique, of course, is only valid for a well crystallized phase, such as Allen postulates, since a less perfect, but still completely crystalline phase will tend to have smaller peak intensities.

We have determined experimentally that sphene can be detected when present in quantities at least as small as 0.5 percent, thus verifying Dr. Allen's observations. To do this, we weighed out samples containing ½%, 1%, and 2% of a powdered sphene crystal. The remainder of each sample was composed of glass made from part of the same sphene crystal by heat treatment. The glass was amorphous, as tested by X-ray diffraction. Each sample was thoroughly mixed, then loaded into a glass capillary tube of internal diameter 0.3 mm and exposed for two hours in a 57.3 mm diameter powder camera. The 6 strongest lines of the sphene pattern are barely visible in the pattern obtained from the ½% sample. These lines are stronger in patterns obtained from the other two samples, and a total of 18 lines is visible in the pattern obtained from the 2% sample. The weakness of these lines relative to the intense amorphous band leaves no doubt but that the bulk of each sample is amorphous.

In closing, we wish to make a plea for more mineragraphic work on titanium minerals and their alteration products. In reflected polarized light, the possi-

bilities for distinguishing sphene, rutile, anatase, and brookite are greatly enhanced. Even when specific identifications cannot be made owing to the fine grain of aggregates, it is sometimes possible to recognize the presence of several types of materials that exhibit distinctly different colors, reflectivities, or degrees of anisotropism. Individual grains of each type can be removed from the surfaces and checked by X-ray methods. These then serve as standards for differentiation within the particular suite of materials. We suggest that more widespread use of mineragraphy in studying the alteration products of titanium minerals will do much to clear up the uncertainties encountered in interpreting petrographic, X-ray, and chemical data of the kinds mentioned by Allen.

We wish to thank Mr. Roger L. Borst for taking the x-ray photographs discussed in this note.

STURGES W. BAILEY
EUGENE N. CAMERON

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
May 11, 1957

REFERENCES

1. Allen, Victor T., 1956, Is leucoxene always finely crystalline rutile?: ECON. GEOL., v. 51, p. 830–833.
2. Bailey, S. W., Cameron, E. N., Spedden, H. R., and Weege, Randall J., 1956, The alteration of ilmenite in beach sands: ECON. GEOL., v. 51, p. 263–279.
3. Cannon, H. B., 1949, Economic minerals in beach sands of the southeastern United States: Proc. of the Symposium on Mineral Resources of the Southeastern U. S., University of Tennessee Press, Knoxville, Tenn., p. 202–210.
4. Hartman, James A., 1957, The titanium mineralogy of certain bauxites and their parent materials: Ph.D. thesis, University of Wisconsin.
5. Tyler, S. A., and Marsden, R. W., 1938, The nature of leucoxene: Jour. Sedimentary Petrology, v. 8, p. 55–58.

REVIEWS

Geology of Uranium and Thorium. Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 8–20 August, 1955, Vol. 6. Pp. 825. United Nations, New York. 1956. Price, $10.00.[1] *Contributions to the Geology of Uranium and Thorium by the U. S. Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955.* Compiled by L. R. PAGE, H. E. STOCKING, and H. B. SMITH. Pp. 739. U. S. Geological Survey, Prof. Paper 300, Washington. 1956. Price, $6.00.

The Geneva Conference probably was the most important gathering of scientists and engineers yet sponsored by the United Nations, and it covered all phases of nuclear science. Although only a handful of geologists were among the delegates, and their presentations had to be squeezed into a single day's sessions, nearly 200 authors submitted well over 100 papers for publication in the proceedings of the conference. The contributions by the United States were also collected and printed separately by its Geological Survey.

This record is a monument to a decade of achievement in this field of geological science. Judged at its face value, the publications indicate that (with a few notable exceptions) a large part of this contribution has been made by geologists in the United States, who contributed two-thirds of the papers. National comparisons seem in order, in view of the fact that most work in this field has been closely controlled and supported by the Governments concerned. Half a dozen other countries reported to the Conference on the beginnings of exploration programs for uranium and thorium. Good summaries are given of new vein deposits in France and Portugal. A few other papers are more detailed but undistinguished, and the description of Spanish uranium minerals by R. F. Cellini is simply and completely inconclusive. One of the most important papers in the volume is the comprehensive description of the Shinkolobwe (Belgian Congo) deposit by J. J. Deiriks and J. F. Vaes. The geological and mineralogical relations are well documented by mine maps and photomicrographs. The bare and succinct paragraphing of the authors is a model of objectivity that extends even to their concluding discussions, but does not make for easy reading.

Only a quarter of the 70-odd delegations made any contributions to the volume on gelogy. A review of the important Canadian deposits will be found only in the verbatim record of the panel discussion; apparently no formal paper was submitted. The brief description of the Australian deposits does not do them justice. It is a matter of conjecture as to what extent complete omissions or very restricted discussions are due to security policy or simply to a misunderstanding of the scope of the conference. The omissions occur on both sides of the iron curtain, including the Union of South Africa as well as the US.S.R. and Czechoslovakia. The delegation from the U.S.S.R. included several geologists, but only two papers (on prospecting techniques) were presented. The ensuing oral discussion yielded such nuggets as "Chairman: I have another question from Mr. Lang (Canada): 'Can Mr. Melkov tell us if airborne surveys in the U.S.S.R. have resulted in discovery

[1] Also available in French, Spanish, or Russian.

of important uranium deposits?' Mr. Melkov (U.S.S.R.): 'I have already read out, from the paper prepared by Mr. Baranov, the statement that a number of industrial deposits have been discovered in the Soviet Union by this method!'" The U.S.S.R. delegation presented an extensive exhibit of new minerals (without locality designations), although some of these have since been more or less discredited (Amer. Mineral. **41**, 816; **42**, 307, 442). The U.S.S.R. apparently made rather extensive contributions to some of the other technical sessions.

The geology of uranium and thorium has presented a considerable challenge to the profession. Many pitchblende veins can be interpreted by classical methods, but the relation of this material to the primary ore of the Colorado Plateau is another question. And the thorium-bearing veins of Colorado are such a recent geological discovery that very little is known about them. The oxidized ores of the Colorado Plateau represent a geological type that had been very sketchily studied before the uranium hunt, and the primary ores had been generally recognized for only a very few years before the Conference. The challenge of these problems has been met with a wide range of new approaches to geological mapping. In addition to the expected radiological methods, every sort of sedimentary feature is being quantitatively investigated (e.g., permeability by D. A. Jobin and B. A. Phoenix, isoliths by Y. W. Isachsen, and paleotopography by R. J. Pitman, H. B. Wood and others). J. H. Mackin and D. L. Schmidt make an interesting application of glacial geology and geomorphology to the understanding of placer deposits. The old but confused concept of comagmatic and metallogenic provinces is realistically delineated (and isn't it about time!) by the statistical analysis of R. R. Coats. The combination of these and more conventional methods has solved many problems, but many others remain: L. R. Stieff's careful age work has dealt the final blow to the syngenetic theory for the Colorado Plateau deposits, but the question of the origin of the uranium still makes geologists choose sides.

The stated emphasis of the exploration programs in the U. S. and U. K. is on geological methods. It is gratifying to find that a number of the deposits described here were discovered by geologists of the U.S.G.S. or A.E.C. A. H. Lang also gives some interesting history of the discovery of Canadian deposits by prospectors, and of their relation to professional geologists in the exploration program. However, the exploration program, at least in this presentation of its results, seems to over-emphasize strictly mapping techniques. The volume overflows with maps, including many of unimportant small prospects and other areas of little general geological interest. Even some important deposits of the Colorado Plateau are duplicated in descriptions in two or more papers. The U.S.G.S. editorial requirements have apparently dragged in a large number of superfluous full-page index maps. Photographs, or even diagrams, are nearly nonexistent; just about the only photomicrographs are in the paper by Deiriks and Vaes, and there are no autoradiographs. Clifford Frondel gives an excellent summary of the mineralogy and geochemistry of thorium, but no comparable paper on uranium is included. However, A. D. Weeks' summary of the relations between mineralogy and geology in the oxidation zones of the Colorado Plateau is a beautiful piece of work that partially fills this gap, and should be assigned reading in any economic geology course.

Several of the review articles will be of most interest to the casual reader, particularly those on the Colorado Plateau by R. P. Fischer, on igneous rocks by G. J. Neuerburg, and on the genesis of uranium deposits by V. E. McKelvey and others. The world summary by P. F. Kerr is in a special class, inasmuch as it is prepared for the lay reader. It therefore must include a number of geological generalities such as a diagram of the earth's interior, but it is difficult to understand why it gives such details as a complete list of radioactive minerals in the Bancroft

pegmatite. Although some attempt is made to make the language non-technical, the statements of concentration must be very confusing to someone without a large table of conversion factors: in two pages uranium concentrations are given in grams per ton, parts per million, per cent uranium, per cent U_3O_8, and pounds U_3O_8 per ton. Further, "Urey indicates that uranium is the least common element in the earth, having an atomic abundance of 0.0002 (Si equals 10,000)." Actually this value is derived ultimately from H. S. Brown, and refers to the composition of an average meteorite. A feature that recommends Kerr's paper is that it includes a review of all the literature. It is also stated to cover most of the papers of the conference, but many of these seem not to have been taken into account: R. Cavaca on Mozambique, M. G. White on Serra de Jacobina, and several important contributions on oxidation relations in the Colorado Plateau deposits. Kerr's paper includes a two-page summary of the origins of radioactive ore deposits, and a selected bibliography of one hundred references.

Each of the two publications has its advantages. The U.S.G.S. volume, besides being less expensive, is logically arranged and contains abstracts and indexes. A paper on the analytical chemistry of uranium and thorium has been added. On the other hand, the U. N. volume includes a few good papers on foreign deposits, such as that on Shinkolobwe, and also Kerr's review of the world literature.

The published results of this conference demonstrate its value in easing the world exchange of information and in precipitating a world-wide appraisal of the current situation in this important field. The conference should serve as a model for future conferences on radioactive materials, and perhaps others on less spectacular but equally important elements such as phosphorus, iron or titanium.

WILLIAM T. HOLSER

INSTITUTE OF GEOPHYSICS,
UNIVERSITY OF CALIFORNIA,
LOS ANGELES, CALIFORNIA,
July 17, 1957

Geologicheskaya Literatura SSSR. 1956, No. 1. Quarterly. Moscow (Gosgeoltekhizdat), 1956. 55 pp. Price 3r. 45k. (50 cents).

For many years there has been published in Moscow an annual Bibliography listing the works on the geology of the U.S.S.R. received by the All-Union Geological Library. To speed up research, this reference journal is henceforth to be issued in quarterly parts. The first number in the new format, covering Russian literature catalogued in January–March 1956, contains 1,190 entries which are grouped under subjects (with sub-headings) in the following proportions: generalities including history and personalia, 136; physical geology, 97; regional geology, 177; palaeontology, 131; geochemistry, 15; laboratory techniques and chemical analyses, 78; mineralogy and crystallography, 92; petrology, 102; hydrogeology and engineering geology, 48; prospecting, 146; economic geology including coal and oil, 168. If the recent improvement in the availability of Soviet geological literature maintains, this index will stimulate a wider recognition by western geologists of the scientific work executed by their Russian colleagues.

Geology and Mineral Resources of the Ivanpah Quadrangle, California and Nevada. By D. F. HEWETT. U. S. Geological Survey Prof. Paper 275. Pp. 172; figs. 58; pls. 2; tbls. 8. Washington, D. C., 1956. Price $2.50.

The field work for this publication, the foremost of D. Foster Hewett's several excellent contributions to the geology of the Mojave Desert, was begun in the early

1920's primarily as a regional study of metallic mineralization. Although much of the volume is thus devoted to economic geology, coverage of the striking stratigraphic and structural features of the quadrangle is sufficiently thorough to elicit the keen interest of geologists in general.

Of especial stratigraphic significance are the author's descriptions of the type sections of the late Precambrian Pahrump series; of an east-to-west transition of Cambrian units from the section characteristic of the Grand Canyon region to the much thicker sequence of the Death Valley region; and of the southwestward extension into California of Mesozoic formations from the Colorado Plateau province.

Accompanying the report are a handsome geologic map and fault classification map, both of which indicate an extreme degree of deformation in the area by thrusting, of both Laramide and Tertiary ages, and by normal faulting. Clearly shown is the spatial relationship of the metallic mineralization to the Laramide thrusts and to bodies of quartz monzonite that locally are intrusive into thrusts.

Perhaps the most intriguing and provocative feature of the report is the author's description of a great late Tertiary plate thought to have been thrust eastward for very large distances into the quadrangle, where it presumably once covered an area of about 500 square miles. In contrast with the Laramide thrusts, which are almost continuously exposed, the Tertiary thrust is now evidenced mainly by widely and irregularly distributed outliers, or klippen, of crystalline rocks, some resting upon Tertiary strata and others upon older crystalline rocks. As the roots of the proposed thrust remain undetected both within and west of the Ivanpah quadrangle, an alternative view—that the outliers are the products of several smaller thrusts and/or locally have slid into place as gravity features—has been entertained by some geologists. The author, however, presents his case vigorously and lucidly.

The uniformly high quality of the author's mapping, descriptions, and interpretations is all the more impressive to the reader who is aware that 3,900 square miles of difficult country was covered under very trying field conditions and at the rate of at least 6 square miles of pre-Quaternary geology a day. In pleasant contrast with most geologic treatises today, this report clearly reflects the author's deep interest in the history of his chosen area and his warm friendships with many of its inhabitants.

LAUREN A. WRIGHT

CALIFORNIA DIVISION OF MINES,
LOS ANGELES, CALIFORNIA,
July 8, 1957

Principles of Stratigraphy. By CARL O. DUNBAR and JOHN RODGERS. Pp. 356; figs. 123; tables 19. John Wiley and Sons, New York, 1957. Price, $10.00.

This long awaited book, in size $7\frac{1}{2} \times 10$ inches, is dedicated to Professor Charles Schuchert whose work at Yale was taken over by Professor Dunbar, and who, with Professor John Rodgers, instituted a course at Yale entitled "Principles of Stratigraphy." This book is the outcome of that course. It represents the collaboration of two authors with different backgrounds of experience and in part with different points of view.

The book is made up of 4 parts. Part I, the Environments of Deposition, covers sedimentary processes, marine, non-marine and mixed environments. Part II, Basic Stratigraphic Relations, deals with stratification, breaks in the record, and facies and facies changes. Part III, the largest, is entitled Interpretation of Specific Lithotopes and covers sedimentary rock nomenclature, rudites, terrigenous arenites, lutites, red beds, carbonate rocks, and siliceous non-fragmental rocks.

Part IV, Synthesis, deals with the local section, correlation, the stratigraphic system, and broad patterns in the distribution of sedimentary rocks. There is a bibliography and author index of 22 pages, and a subject index. There are many excellent illustrations and the large page size permits them to be displayed effectively.

As the title states, the book deals only with the principles of stratigraphy, and the customary systematic accounts of stratigraphy records are omitted. The authors have succeeded in presenting a lucid account of the principles and have drawn upon excellent examples to illustrate them. The book is printed, bound, and edited with the customary Wiley thoroughness. It should constitute the outstanding text book on the principles of stratigraphy.

Prospektion von Uran-und Thoriumerzen. By G. ZESCHKE. Pp. 76; figs. 26; tables 6. E. Schweizerbart'sche Verlag. Stuttgart, 1956. Price, D.M. 13.

This little book is written by a geologist experienced with radioactive ore deposits and is meant for the lay reader as well as trained technicians in geology, physics, chemistry and metallurgists. It covers the geology and geochemistry of uranium and thorium ores, mineral identifications and field methods. It tells where and how to prospect for such minerals, and the use of the Geiger counter, scintillometer, fluorescence, and radiometric analyses. It gives a long identification table of uranium and thorium minerals and their properties. It carries an incomplete bibliography of 172 items of which most are of North American and English origin.

Geologic Field Methods. By JULIAN W. LOW. Pp. 489; figs. 214; tables. Harper & Bros., New York, 1957. Price, $6.00.

This new manual on field methods gives the viewpoint of a practicing research geologist of the California Company. It is meant both for the professional geologist and as a text book (for which a price of $4.50 is set for quantity orders).

Its 10 chapters are 1) Introduction to Surface Geological Investigations, 2) Organization of Field Work, 3) Living and Working Out of Doors, 4) Field Mapping, 5) Topography and Areal Geology, 6) Structural Field Work, 7) Stratigraphic Field Work, 8) Mineral Exploration, 9) Subsurface Methods, 10) Geologic Illustrations. A 35-page Appendix gives various mathematical tables, conversion charts and correction charts used in geologic field work.

The volume deals primarily with field methods rather than geologic principles. With this book an inexperienced student supposedly can proceed with field work without prior instruction; the procedures are detailed step by step. It is clearly and plainly written and adequately illustrated. It should prove a very useful text book for courses in field geology.

Geology of India and Burma, 3rd Edit. By M. S. KRISHNAN. Pp. 555; figs. 14; map. Higganbothams Ltd., Madras, India, 1956. Price, Rs. 22/8.

The first edition of this book was published in 1943 and the second edition in 1949. Since then there has been much advance in geologic knowledge of India. The Geological Survey has been greatly expanded, and the Government has been sponsoring research in the universities and in its new research centers. In addition, territorial changes have taken place with the formation of new states and this has necessitated changes in geographic designations; also new spelling for many place names has been introduced. The preface carries a list of all these changes.

This edition carries much revision of chapters and there has been added a summary of the stratigraphy of the Gondwana System in the southern continents, since India is a part of the old Gondwanaland. The book also carries a colored copy of the new geologic map of India-Pakistan-Burma, on a scale of one inch = 96 miles. A geologic map of Ceylon has also been added.

The treatment is generally the same as in the previous edition. The chapters cover physical geology, structure and tectonics, review of Indian stratigraphy, the Archaean group and their mineral resources, which include antimony, chrome, columbite, copper, gold, iron ore, lead-zinc, manganese, molybdenite, monazite, titanium, tungsten, asbestos, beryl, corundum, gem stones, graphite, kyanite, magnesite, mica, and steatite. Following chapters describe the Cuddapah and Vindhyan Systems, the Gondwana group, and the Paleozoic, Mesozoic, Cenezoic, Deccan traps, and Glaciation. Selected bibliographies follow each chapter.

The book is nicely printed and bound, and constitutes a compact summary of the geology of this large area.

The Living Rocks. By STÉVAN CÉLÉBONOVIC, translated by JOYCE EMERSON and S. A. POCOCK. Pp. 94. Philosophical Library, New York, 1957. Price, $6.00.

This book is a first volume of Art and Nature Series photographed and devised by Stévan Célébonovic, with further volumes to follow. It contains a preface by André Maurois and a commentary by Geoffrey Grigson.

The book carries an $8 \times 11\frac{1}{2}$ inch page and is made up almost wholly of full-page size pictures. It contains 24 such plates of minerals, and 64 of fossils, with 14 pages of commentary, along with legends for the plates. The photography is beautifully done and the reproduction is excellent. The choice of subject matter for the plates is highly artistic. It is a book one can linger over and study with enjoyment.

The Exploration of the Colorado River. By JOHN WESLEY POWELL. Pp. 138. Univ. of Chicago Press, 1957. Price, $3.75.

This book is abridged from Powell's classical first edition of 1875 dealing with the exploration of the Colorado River and its tributaries, and of the first trip through the Grand Canyon. It carries a foreword by Leonard Carmichael, Secretary of the Smithsonian Institution, and an introduction by Wallace Stenger.

The original volume consisted of three parts: 1) Powell's explorations in 1869–70, 2) Powell's monograph on the exploration and geology of the Colorado River Valley, and 3) the monographs by Coues and Goode on the Colorado rodents. The last two parts have been omitted from this volume, which contains Powell's account of the first voyage through the canyons of the Colorado with a few of his original illustrations.

Powell's trips were among the great feats of early western American exploration and his journal is a tale of thrilling adventure associated with scientific discovery. It has become a classic of Western Americana, and required reading in many departments of Geology. This abridged edition offers opportunity for all to become acquainted with one of the thrilling exploratory adventures of the West.

The hundreds of miles of canyon exploration are considered in 8 chapters, dealing with as many sections of the route; the last two are about the Grand Canyon and the Rio Virgen. Here are vivid descriptions of the colossal canyons, the tale of 4 boats and 10 men who became reduced to 6, the hardships and privations, the Indians, and sketches of the geology of this awe-inspiring country that is now preserved in National Parks.

Introduction à L'Étude des Roches Métamorphiques et des Gites Métallifères. By PIERRE LAFFITTE. Pp. 338; figs. 16; tables 10. Masson et Cie., Paris, 1957. Price, 4000 fr.

The author of this book is Director of the Bureau of Geologic, Geophysical, and Mining Research of metropolitan France. It carries a preface by E. Raguin, well known as the author of a text book on economic geology. The title carries a subtitle "Physico-Chimie et Thermodynamique."

The author brings to this subject a background training in physical chemistry and studies of metamorphic rock formations in the Alps and in Brittany. He now brings together modern concepts of chemical equilibria, solidification diagrams and thermodynamics to the study of petrogenesis. He divides his work into 4 parts. Part I, Physical-Chemical Generalities, with two chapters deals with elementary particles. Part II, the Chemical Composition of Rocks, has three chapters on chemical generalities, chemical analyses, and petrochemical calculations and representations. Part III, Thermodynamics, is composed of four chapters on thermodynamic generalities, description of some phases, equilibrium between different phases, and hydrothermal problems. Part IV, also of four chapters, is entitled Petrology of Metamorphic Rocks. These are generalities on Metamorphism, method of study of Metamorphic rocks, equilibrium in Metamorphism, and movements of material. The last chapter goes into metamorphic differentiation, metasomatism, the cycle of water, and metamorphism and metallogeny. He believes that metamorphic differentiation can account for many examples of ore deposits, without calling on deep-seated sources of mineralizing fluids. Extensive bibliographies follow each part.

The book assembles a great deal of petrologic information and has been carefully prepared and written as would be expected of Dr. Laffitte. It should prove a useful French text book and a general reference work on metamorphism.

BOOKS RECEIVED

JAMES M. ALLEN AND JOHN W. SALISBURY

Experiments on the Possible Relationship Between Soil Resistivity and Dowsing Zones. S. W. TROMP. Pp. 35; pls. 41. Foundation for the Study of Psycho-Physics, Leiden, Holland, 1955 (1957). *A follow-up of the author's "Psychical Physics" (1947) depicting objectively by text and many charts certain correlations between locations indicated by nonprofessional dowsers and magnetometer and resistivity surveys over the same ground; checked by skin cardiograms of performing dowsers; interesting correlations.*

The Faunal Connections Between Europe and North America. C. H. LINDROTH. Pp. 344; figs. 74. Price, $15.00. John Wiley & Sons, New York; Almqvist and Wiksell, Stockholm, 1957. *Fresh water and land animal species common to both areas; human transport of animals; pre-human relationship between Palaearctic and Nearctic faunas; extensive bibliography.*

Bureau de Recherches Minières de L'Algérie, Bull. 4. Pp. 81, illust. Alger, 1957. *Geology and copper, lead, and zinc mineralization of Bou Soufa and Oued el Kebir at Caballo, by G. Tayeb and M. M. Rerkell and Waline; metallogenetic studies by J. Ranoux.*

Economia Minera. Edicion Extraordinaria—1ér Aniversario. Nos. 1 and 2. Pp. 262. Buenos Aires, Argentina, 1957. *Papers on the mineral production and resources of Argentina.*

Bulletin des Seances. Tome II, No. 6. Pp. 386, pls. 12; figs. 18. Price, 150 francs. Academie Royale des Sciences Coloniales, Bruxelles, Belgique, 1956. *Papers in geology, medicine, sociology, etc. In French and Flemish.*

Geology of the Antler Creek Area Cariboo District, British Columbia. A. SUTHERLAND BROWN. Pp. 103; pls. 9; figs. 23; tbls. 4. British Columbia Department of Mines, Bull. 38, Victoria, 1957. *Structure, stratigraphy, petrology and economic geology of the Cariboo gold-quartz area. Two mines have an annual production of 1½ million dollars in gold.*

British Guiana Geological Survey, Annual Report for 1955. G. M. STOCKLEY, Director. Pp. 129; maps. Price, $2.00. Georgetown, 1956 (1957).

Ceylon, Administrative Report of Government Mineralogist for 1956. L. J. D. FERNANDO. Pp. 24. Price, 60 cts. Colombo, 1957. *Non-metallic minerals, water supply and summary of general geology of 5 sheets.*

The Structure of an Archean Area: Orijärvi, Finland. HEIKKI V. TUOMINEN. Pp. 32; pls. 6; figs. 16. Bulletin de la Commission Géologique de Finlande. No. 177. Helsinki, 1957. *Geology of metamorphic terrain in S. W. Finland. Geologic, aeromagnetic and electromagnetic maps accompanying the report. In English.*

Bericht über das Vorkommen von Uran in Baden-Württemberg. FRANZ KIRCHHEIMER. Pp. 127; pls. 6; figs. 12. Abhandlungen des Geologischen Landesamtes in Baden-Württemberg. Heft 2. Freiburg, Germany, 1957. *Geology and history of uranium production in the famous Freiburg region. In German.*

Geology of the Bawku-Gambaga Area. E. A. REDMONDS. Pp. 54; figs. 11, maps 3. Gold Coast Geological Survey Bull. 19. Accra, Gold Coast, 1956 (1957). *General geology, geologic history, petrography of schists, petrogenesis, soils, water resources.*

Depositional Environment of the Wreford Megacyclothem (Lower Permian) of Kansas. DONALD E. HATTIN. Pp. 145; pls. 22; figs. 6; tbls. 2. Kansas Geological Survey Bull. 124, Lawrence, 1957. *Complete stratigraphic description of the Wreford limestone and adjacent shales; nature and significance of the sedimentary rock types.*

Sands of the Merrimack Valley. Part XVI, Mineral Resources Survey. LAWRENCE GOLDTHWAIT. Pp. 19; pl. 1. New Hampshire State Planning and Development Commission, Concord, 1957. *Geologic history of the Merrimack Valley, nature of the sands occurring there and their uses.*

Precambrian Geology and Mineral Resources of the Brier Hill Quadrangle, New York. RICHARD V. DIETRICH. Pp. 118; pls. 21; figs. 7; tbls. 7. New York State Museum and Science Service, Bull. 354. Albany, 1957. *Regional geology of a complex metamorphic and igneous terrain in northern New York. Building and road materials are the only economic products; unusual group of igneous rocks.*

Petrology of the Lower Mesozoic Rocks of the Wellington District. J. J. REED. Pp. 55; pl. 1; figs. 36; tbls. 8. New Zealand Geological Survey, Bull. 57. Wellington, 1957. *Stratigraphy, structure and petrography of the sedimentary and volcanic rocks of the southern tip of North Island.*

Ontario Department of Mines Sixty-fifth Annual Report. Vol. LXV, Pt. 3, 1956. Pp. 121; figs. 10; maps 2. Toronto, 1957. *A Sudbury basin number with three papers: Geology of the Sudbury Basin by J. E. Thomson; Glowing Avalanche*

Deposits of the Sudbury Basin by Howel Williams; and Copper Cliff Rhyolite in McKim Township, by T. C. Phemister. The Basin is more complicated than supposed. The Sudbury intrusion as a lopolith is untenable.

Annual Report of the Geological Survey Somaliland Protectorate. Pp. 13. Price, Shs. 2/50. 1957. *Operations of the geological survey from April 1956 to March 1957. Mineral exports were 1680 lbs. columbite, tantalite and 16 tons of beryl; investigations of cassiterite and gypsum.*

Mineralogy of the Barberton Gold Deposits. J. E. DE VILLIERS. Pp. 60; pls. 10. South Africa Geological Survey Bull. 24, Pretoria, 1957. *Microscopic study of ores with arsenopyrite and pyrrhotite, pyritic ores, lead-bearing ore, antimonial ore, and gold concentrates. The first three are part of same mineralization.*

Bulletin of the Geological Survey of Taiwan. No. 8. Pp. 115; pls. 10; figs. 6; tbls. 12. Taipei China, 1956. *Five papers concerning some aspects of the stratigraphy and paleontology of the island of Formosa.*

A Preliminary Report on the Stratigraphy of the Uranium-Bearing Rocks of the Karnes County Area, South-Central Texas. D. HOYE EARGLE and JOHN L. SNIDER. Pp. 30; figs. 5. Price, 50 cts. University of Texas, Bureau of Economic Geology Report of Investigations No. 30, Austin, 1957. *A preliminary investigation of the stratigraphy and correlation of the potentially uranium-producing beds of the area from drill holes and surface exposures. Prepared in cooperation with the U. S. Geological Survey.*

Introduccion a la Memoria del Ministerio de Minas e Hidrocarburos (Presentada al Congreso Nacional en Sus Sesiones Ordinarias de 1957). Pp. 96; pls. 4; figs. 12; tbls. 27. Caracas, Venezuela, 1956. *Record of mineral and oil production for 1956. Includes production figures for iron, gold, diamonds, coal, pyrite, phosphates, nickel, manganese, and uranium. Estimates of reserves and future production.*

Geology and Economic Resources of the Ohio River Valley in West Virginia. Pp. 149; pls. 2; figs. 200; tbls. 19. West Virginia Geological Survey, Vol. XXII, Morgantown, W. Va., 1956. *Detailed areal study in three parts. Part I, by A. T. Cross and M. P. Schemel, deals with general geology, origin and nature of the rocks and sediments, their stratigraphy, paleontology, and structure. Part II, also by Cross and Schemel, is Economic Resources with chapters on origin, occurrence, and uses of coal, oil and gas, rock salt and brines, clay, sand and gravel, limestone and sandstone, iron and sulfur, and water. Part III, by C. W. Carlston and G. D. Graeff, Jr., of the U.S.G.S., deals with ground-water resources. Minimum of dry description as with the other two parts. All aspects of ground-water covered from its sources and movement to permeability of water-bearing materials.*

Major Activities in the Atomic Energy Programs January–June 1957. Pp. 257; figs. 15; tbls. 28. U. S. Atomic Energy Commission, Washington, D. C., 1957.

Molybdenum—A Materials Survey. WILMER MCINNIS. Pp. 77; tbls. 22. Bur. of Mines Inf. Circular 7784. Washington, D. C., 1957. *This is the 13th Materials Survey published by the Bureau of Mines, 12 being under the direction of the National Security Resources Board, this one under the director of the office of Defense Mobilization. Covers history, geology, resources, technology, production uses, trade, statistics, controls.*

Colorado School of Mines—Golden, 1957.

Vol. 52, No. 2. Bibliography of Fossil Algae: 1942–1955. J. HARLAN JOHNSON. Pp. 92. Price, $1.00. *Indexed by genera, family, etc., geologic age, subject, and geography. Extensive annotated bibliography.*

Vol. 52, No. 3. Behavior of Materials in the Earth's Crust. Pp. 306; figs. 137; tbls. 5. Price, $2.00. *Papers and discussions from the Second Annual Symposium on Rock Mechanics. Basic concepts and practical application to mining.*

Geological Survey of Egypt—Cairo, 1955–56.

Geology of El-Mueilha-Dunqash District. M. F. EL-RAMLY and D. M. AL-FAR. Pp. 44; pls. 17; tbls. 5. Price, P.T. 90. *Two maps, scale 1:100,000.*

The Dolomite and Dolomitic Rocks of Gebel 'Atâqa. M. A. Z'ATOUT. Pp. 27; pls. 9; tbls. 10. Price, P.T. 60. *Locations and quarrying possibilities. Map, scale 1:100,000.*

Geology of Wadi Garf District. M. SABER MANSOUR and F. A. BASSYUNI. Pp. 34; pls. 17; figs. 5; tbl. 1. Price, P.T. 100. *Economic chromite and feldspar. Map, scale 1:100,000.*

Illinois Geological Survey—Urbana, 1957.

Circ. 225. Ground Water Geology in South-Central Illinois. L. F. SELKREGG, W. A. PRYOR and J. P. KEMPTON. Pp. 30; figs. 7. *Probable location of aquifers.*

Rept. of Inv. 200. Chemical Analyses of Illinois Limestones and Dolomites. J. E. LAMAR. Pp. 33; tbls. 2. *More than 700 chemical analyses of Illinois limestones and dolomites.*

Rept. of Inv. 201. Types of Late Cenozoic Gastropods in the Frank Collins Baker Collection, Illinois State Geological Survey. A. BYRON LEONARD. Pp. 23; pls. 4. *34 types.*

North Dakota Geological Survey—Grand Forks, 1957. Circ. 5. (Sixth Revision.) Pp. 119. *Contains information from all well records received at the N.D.G.S. through April 15, 1957. Well information includes: company, well name, location, permit number, elevation, total depth, completion data and initial production. Corrections and additions make all previous issues of Circular 5 out of date.* **Production Statistics and Engineering Data Oil in North Dakota First Half 1957.** Pp. 40. *Statistics of pools.*

U. S. Geological Survey—Washington, D. C., 1957.

Prof. Paper 274-M. Metamorphism and the Origin of Granitic Rocks, Northgate District, Colorado. T. A. STEVEN. Pp. 335–377; figs. 4; pl. 8. *Discussion of the progressive metamorphism, granitization, and local rheomorphism of a layered sequence of Precambrian rocks, and of the later emplacement and denteric alteration of an unrelated granite stock.*

Prof. Paper 282-B. River Channel Patterns: Braided, Meandering and Straight. LUNA B. LEOPOLD and M. GORDON WOLMAN. Pp. 85; figs. 30; tbls. 14. *Continuation of physiographic and hydraulic studies of rivers. Channel cross section and pattern ultimately controlled by discharge and load provided by the drainage basin; braiding does not necessarily indicate excess of total load, and mechanics which may lead to meandering operate in straight channels. Excellent treatise.*

Prof. Paper 283. Mississippian Cephalopods of Northern and Eastern Alaska. MACKENZIE GORDON, JR. Pp. 61; pls. 6; figs. 26; tbls. 2. *Descriptions and illustrations of 43 nautiloids and ammonoids and correlation of the assemblages with European Carboniferous goniatite zones.*

Prof. Paper 290. Geology and Mineral Resources of the Congonhas District Minas Gerais, Brazil. PHILIP W. GUILD. Pp. 90; figs. 35; pls. 9. *General geology, geologic history, and metamorphism of Precambrian sediments and igneous*

rocks and sediments containing unaltered itabirite, and high-grade hematite ores in reserves of 150 million tons; discussion of origin of iron sediments.

Prof. Paper 294-A. North America Mesozoic Charophyta. RAYMOND E. PECK. Pp. 44; pls. 8; figs. 7; tbls. 2. *The 35 species and 12 genera of presently known United States Mesozoic charophytes are described and illustrated. Seventeen species and one genus are new. Their common occurrence, worldwide distribution, and easy identification make them helpful in subdividing nonmarine strata.*

Bull. 1000-F. Principles of Geochemical Prospecting. H. E. HAWKES. Pp. 225–255. *Discussion of three types of deep-seated primary anomalies—local variation of earth's crust, hydrothermal rock alteration, and gaseous alterations; and of secondary anomalies through weathering, water, or ice; most successful prospecting is bases on analyses of soils or vegetation.*

Bull. 1000-G. Geochemical Prospecting Abstracts July 1952–December 1954. JANE EBNER ERIKSON. Pp. 38. Price, 20 cts. *A review of recent literature on the techniques of geochemical, biogeochemical and geobotanical prospecting.*

Bull. 1019-F. Selected Annotated Bibliography of Thorium and Rare-Earth Deposits in the United States Including Alaska. KATHERINE L. BUCK. Pp. 20; pl. 1; fig. 1. Price, 40 cts. *Uses, location of ore deposits and resumé of the literature dealing with thorium and the rare earth metals in the United States and Alaska.*

Bull. 1021-L. Geology of the Area East and S.E. of Livingston, Park County, Montana. PAUL W. RICHARDS. Pp. 385–438; figs. 9; pls. 3. *Geography, geology of metamorphic and igneous rocks and of Paleozoic, Mesozoic, and Quaternary formations; economic geology of oil, gas, coal, gypsum, bentonite.*

Bull. 1024-I. Tungsten Deposits in the Fairbanks District Alaska. F. M. BYERS, JR. Pp. 36; pls. 6; fig. 1. Price, $1.00. *Description of scheelite deposits in metamorphosed limestone, calcareous mica schist, quartz pegmatites and gold quartz veins; suggestions for further prospecting.*

Bull. 1029-A. Annotated Bibliography of the Analytical Chemistry of Niobium and Tantalum January 1935–June 1953. FRANK CUTTITTA. Pp. 65. Price, 25 cts.

Bull. 1032-C. Geology of the Wood and East Calhoun Mines Central City District Gilpin County, Colorado. AVERY A. DRAKE, JR. Pp. 40; plates 4; figs. 13; tbls. 7. Price, $1.00. *Ore shoots containing gold, silver and pitchblende occur in quartz sulphide veins filling easterly and northeasterly trending faults in Precambrian gneisses. Bostonite porphyry dikes of Tertiary age intrude the gneisses. Future outlook is not bright.*

Bull. 1036-L. A Field Chromatographic Method for Determination of Uranium in Soils and Rocks. CHARLES E. THOMPSON and H. W. LAKIN. Pp. 11; figs. 2; tbls. 6. Price, 15 cts. *A fast simple method for uranium analysis in the field.*

Bull. 1042-I. A Reconnaissance Study of the Beach Sands of Puerto Rico. ROBERT B. GUILLOU and JEWELL J. GLASS. Pp. 33; pls. 1; figs. 4; tbls. 6. Price, 60 cts. *200,000 to 300,000 tons of magnetite are indicated; ilmenite and chromite are also found. Sphene is a minor constituent of the sands and zircon is rare.*

Bull. 1045-B. Core Logs from Two Test Holes Near Kramer, San Bernardino, California. D. D. DICKEY. Pp. 63–79; fig. 1; pl. 1. *Detailed logs of stratigraphy of Quaternary and Tertiary sediments.*

Bull. 1047-A. Coal Geology of the White Oak Quadrangle Magoffin and Morgan Counties, Kentucky. W. L. ADKISON. Pp. 23; pls. 4; figs. 6; tbls. 2. *Coal of high volatile bituminous rank and small amounts of cannel coal in Pennsylvanian rocks. Total estimated original reserves of 92 million tons in beds more than 14 inches thick.*

Bull. 1049. Bibliography of North American Geology 1940–1949, Part 1, Bibliography, Part 2, Index. RUTH R. KING, EMMA M. THOM, ELISABETH S. LOUD and MARJORIE HOOKER. Pp. 2205. Price, $1.50. *The customary decennial bibliography and index, greatly enlarged.*

Bull. 1054. Bibliography of North American Geology, 1954. RUTH REECE KIND and others. Pp. 273. Price, $1.50.

Bull. 1059-A. Selected Annotated Bibliography of the Geology of Uranium-Bearing Coal and Carbonaceous Shale in the United States. T. M. KEHN. Pp. 1–28.

Bull. 1059-B. Selected Annotated Bibliography of the Geology of Uranium-Bearing Phosphorites in the United States. DIANE CURTIS. Pp. 29–58.

Bull. 1066-A. Geophysical Abstracts 168, January–March, 1957. MARY C. RABBIT et al. Pp. 1–94.

Water-Supply Paper 1371. Ground-Water Resources of the Ainsworth Unit, Cherry and Brown Counties, Nebraska. J. C. CRONIN, T. G. NEWPORT, and R. A. KRIEGER. Pp. 120; figs. 20; pls. 2; tbls. 7. *Geology, water-bearing formations, hydrologic properties, ground water, chemical quality.*

Water-Supply Paper 1411. The Deep Channel and Alluvial Deposits of the Ohio Valley in Kentucky. E. H. WALKER. Pp. 25. *Only source of large supply of good, cool water of area; in Wisconsin gravels.*

SOCIETY OF ECONOMIC GEOLOGISTS

PROGRAM OF ANNUAL MEETING—ATLANTIC CITY, NOV. 4–6

SCIENTIFIC SESSIONS

Tuesday, Nov. 5, 3:00 P.M. Business meeting of Coal Group, Mandarin Room, Haddon Hall.

Tuesday, Nov. 5, 4:00 P.M. S.E.G. Council meeting, Library of Haddon Hall.

Wednesday, Nov. 6, 12:30 P.M. S.E.G. Luncheon, Wedgewood Room, No. 2, Haddon Hall.

Wednesday, Nov. 6, 1:30 P.M. Presidential Address by C. H. Cady on *Coal Geology and the Coal Industry*, following the luncheon.

(After each paper 5 minutes is allowed for discussion)

TUESDAY AFTERNOON, RUTLAND ROOM

ECONOMIC GEOLOGY—I

MEREDITH E. JOHNSON and JOHN H. MELVIN, *Co-Chairmen*

1. 2:00 Lloyd L. Ames, Jr.: *Chemical analyses of the inclusion fluids in a group of New Mexico minerals*
2. 2:15 R. G. Petersen,* J. C. Hamilton, and A. T. Myers: *Occurrence of rhenium, associated with uraninite, in Coconino County, Arizona*
3. 2:35 R. M. Garrels, P. B. Hostetler,* C. L. Christ, and A. D. Weeks: *Stability of uranium, vanadium, copper, and molybdenum minerals in natural waters at low temperatures and pressures*
4. 2:50 M. L. Jensen: *Significance of S^{32}/S^{34} ratios on the origin of sulfides in uranium deposits of the Colorado Plateau*
5. 3:10 John A. S. Adams* and Keith Richardson: *Thorium, uranium, and potassium contents of bauxite*
6. 3:25 H. L. Barnes: *Trace-element distribution in shales near the Hanover, New Mexico, mining areas*
7. 3:45 A. E. J. Engel and C. Patterson*: *Isotopic composition of lead in Leadville limestone, hydrothermal dolomite, and associated ore*
8. 4:05 Heinrich D. Holland: *Thermochemical data, mineral associations, and the Lindgren classification of ore deposits*
9. 4:25 Charles T. Illsley: *Hydrogeochemical exploration for uranium in the Mount Spokane area, Washington*

* Speaker.

WEDNESDAY MORNING, VERNON ROOM

ECONOMIC GEOLOGY—II

G. M. SCHWARTZ and H. G. GUNNING, *Co-Chairmen*

1. 8:30 John B. Mertie, Jr.: *Geologic occurrence of monazite and zenotime in the Southeastern States*
2. 8:50 Victor T. Allen: *Minerals in laterites in the State of Bolivar, Venezuela*
3. 9:00 H. D. Goode * and C. S. Robinson: *Lithologic and structural controls of uranium deposition in the Hulett Creek mining area, Crook County, Wyoming*

9:15 Stewart R. Wallace,* David C. Jonson, Robert A. Navias, and Stanley A. Skapinsky: *Ring-facture intrusion and mineralization at Climax, Colorado: a preliminary report*

9:35 F. G. Snyder * and J. W. Odell: *Mineralized submarine slides in the Southeast Missouri lead district*

9:55 Bronson Stringham: *Relationship of ore to porphyry in the Great Basin*

10:15 Joe Webb Peoples,* Norberto S. Fernandez, S. Samaniego, and Miguel de la Cruz: *Chromite in the Zambales Range, Luzon*

10:35 D. F. Davidson * and R. A. Gulbrandsen: *Selenium in the Phosphoria Formation, Idaho, Wyoming, Utah, and Montana*

10:50 Henry L. Jicha, Jr.: *Hydrothermal zoning of lead in the manganese ores of the Luis Lopez district, Socorro County, New Mexico*

11:05 Alice D. Weeks,* Alfred H. Truesdell, and Joseph Haffty: *Nature of the ore boundary and its relation to diagenesis and mineralization, Uravan district, Colorado*

11:25 Ned M. Smith: *Selection of quarry sites in the dimension limestone belt of Indiana*

11:40 Margaret A. Parker: *Application of punched-card analysis to limestone exploration*

TUESDAY MORNING, MANDARIN ROOM

COAL—I

JOHN W. HUDDLE and IRVING A. BREGER, *Co-Chairmen*

1. 9:00 John A. Harrison: *Comparison of methods of petrographic analysis and their relation to the coking character of coal*
2. 9:20 Alexander R. Cameron: *Maceral groups characterizing the Elkhorn seam at Evanston, Kentucky*
3. 9:40 Norman Schapiro: *Petrographic analyses of the various density separations of coal*
4. 10:00 Russell R. Dutcher,* Charles L. Trotter, and William Spackman, Jr.: *Petrographic examination of coals from the Arctic Slope of Alaska*
5. 10:20 Lewis H. King * and Alex R. Cameron: *Petrographic examination of coal pellets prepared by compressing plasticized particles of crushed coal*

* Speaker.

6. 10:40 Alonzo W. Quinn * and Herbert D. Glass: *Rank of coal and metamorphic grade of rocks of the Narragansett Basin of Rhode Island*
7. 11:00 S. A. Friedman: *Distribution, thickness, and origin of sinuous sandstone lenses of the Allegheny Series, Vigo County, Indiana*
8. 11:20 Taisia Stadnichenko: *"Clarke" concept and its use in geochemistry*
9. 11:35 Donald Gednetz and Harold R. Wanless *: *Environmental mapping of the St. David cyclothem, eastern and western interior coal basins*

TUESDAY AFTERNOON, MANDARIN ROOM

COAL—II

RALPH J. BERNHAGEN and LEWIS H. KING, *Co-Chairmen*

1. 2:00 George H. Denton: *Plant microfossil assemblages in Lower Allegheny coal beds of northeastern Ohio, western Pennsylvania, and northern West Virginia*
2. 2:20 Marcia B. Winslow: *Plant megaspores from coals of Illinois*
3. 2:40 Russell A. Brant: *Coal-resources studies in Ohio*

3:00 BUSINESS MEETING, GROUP ON COAL (GSA)

JAMES M. SCHOPF and CHARLES E. WIER, *Co-Chairmen*

Report on Gordon Conference. William Spackman, Jr.
Report on Valkenburg Meeting. Sabri Ergun
Reports of Committees:
Bibliography. Irving A. Breger, *Chairman*
Publications. Paul Averitt, *Chairman*
Coal Petrographic Terminology. G. H. Cady, *Chairman*

* Speaker.

SCIENTIFIC NOTES AND NEWS

The Society of Mining Engineers of the American Institute of Mining, Metallurgical, and Petroleum Engineers, has announced that STANLEY D. MICHAELSON, of Salt Lake City, Chief Engineer, Western Mining Division, Kennecott Copper Corp., has been nominated for 1958 President of the Society. He also will serve as Director of AIME.

SIDNEY L. GROFF joined the staff of Montana Bureau of Mines and Geology, Butte, on August 1, as geologist and head of the groundwater branch.

The two Geological Societies of Belgium held a special session on Sept. 20–23, devoted to the study of the Geomorphology and Quaternary Geology of Haute Belgique.

GEORGE VIBERT DOUGLAS, Carnegie Professor of Geology at Dalhousie University, Halifax, N. S., has now retired from the chair and has set up as a Consulting Geologist with an office at 16 Duplex Avenue, Toronto.

WESTON BOURRET, who directs exploration activities for the Utah Construction Company, has been appointed Vice President of Utah Development Company, Utah Construction Company's exploration subsidiary, as well as a director of Lucky Mc Uranium Corporation.

WALLACE G. BELL, senior geologist for Gulf Oil Company at Casper, Wyoming, has joined the staff at the University of Missouri where he will teach structural geology and closely related subjects.

A. I. LEVORSEN, consulting geologist, and GERALD H. WESTBY, president of the Seismograph Service Corp., are new members of the board of trustees of the University of Tulsa.

WALTER CURRAN MENDENHALL died on June 2 at the age of 86 years. He retired in 1943 from the United States Geological Survey after 48 years of service on the Survey Staff. He was a former director of the Survey and an honorary member of the A.A.P.G.

MERLE H. GUISE has been traveling in Mexico and is now at Instituto Allende, Guanajuato, Mexico.

FELIX E. WORMSER has resigned as Assistant Secretary of the Interior. Mr. Wormser has rejoined St. Joseph Lead Co., New York, as vice president, the position he held prior to entering Government service in 1953.

Members of Behre Dolbear & Co. Inc., New York, are on foreign assignments. PARKE A. HODGES and CHESTER M. F. PETERS are in Nicaragua. THEODORE B. COUNSELMAN, ELLIOTT E. CHECK, and B. H. MCLEOD are conducting a mine examination in Chile. A. F. BANFIELD has been in Cuba on a geological mission.

DONALD W. LINDGREN has been appoined chief mining geologist for the Northern Pacific Railway Co. with headquarters at St. Paul, Minn.

K. E. BULLEN, chairman of the Australian National Committee for the International Geophysical Year, will speak to 16 local sections of the Society of Exploration Geophysicists on a tour which will cover most of the United States and part of Canada during September and October.

J. M. RAYNER, Deputy Director of the Bureau of Mineral Resources, Geology and Geophysics left Australia on the 9th of August to spend about two months in the United States and Canada attending various scientific meetings. Mr. Rayner is Vice President of the International Association of Geomagnetism.

C. A. LUVERNE HOGG has resigned the post he had held since 1946 as Deputy Minister of Mineral Resources of the Province of Saskatchewan. He has also resigned the Chairmanship of the Oil and Gas Conservation Board.

E. W. GROVE has been appointed Geologist II at the Yellowknife N.W.T., operation of the Consolidated Mining and Smelting Company of Canada, Ltd.

M. K. ABEL has been appointed Senior Assistant Geologist for Geco Mines, Ltd., Manitouwadge, Ontario.

J. E. GILL, Professor of Geology at McGill University, has been awarded the Willet G. Miller Medal of the Royal Society of Canada for 1956.

C. H. CHARLEWOOD, formerly Chief Geologist, Manitoba Department of Mines and Natural Resources, has been appointed Vice-President of the Heath & Sherwood Drilling, Ltd., Kirkland Lake, Ontario.

Newmont Exploration Ltd., a subsidiary of Newmont Mining Corp., has established a geophysical and metallurgical research laboratory near Danbury, Conn. A. A. BRANT is director of the geophysical section, and the metallurgical section is under the direction of L. J. BECHAUD, JR.

LESTER R. CHILD, Grants Pass, has been appointed to the Oregon Board of Geology and Mineral Industries to fill the vacancy created by the resignation of Neil R. Allen.

OLIVER G. SEYMOUR and PAUL ZIMMER, Iron River, geologists with the M. A. Hanna Co., have received new appointments. Mr. Seymour will be in charge of exploration work in the Michigan district and will spend some time on property examinations and exploration in Latin America, while Mr. Zimmer will be in charge of geological work at the Hanna Co. operating mines.

R. LEE ASTON has resigned as mine geologist of the Tennessee Copper Co. to become plant engineer of the Signal Mountain Division of General Portland Cement Company's operation at Chattanooga.

Y. WILLIAM ISACHSEN has left his position as research geologist at A.E.C.'s Grand Junction Operations Office to serve as technical adviser to the Turkish government in organizing a uranium exploration program. He will serve as a member of the Technical Services Organization with headquarters in Ankara, Turkey.

PLATO MALOZEMOFF, president of Newmont Mining Corp., was awarded an honorary degree of Doctor of Engineering at the annual commencement of the Colorado School of Mines.

WILLIAM H. KING, Denver mining engineer, has been appointed executive officer of the Defense Minerals Exploration Administration's field team in Region III where he will direct DMEA operations in an eight state area. Formerly Mr. King served as superintendent of the Bureau's Denver experiment station.

H. W. STRALEY, III, has moved his offices from 1122 Mercer Street, to the Seneca Trail Building, Honaker Avenue and Walker Streets, both in Princeton, West Virginia. His mailing address remains the same—Box 68, Princeton, West Virginia.

DONALD TOWSE is now in Brazil where he is Project Geologist for Kaiser Aluminio Ltda. His address is Caixa Postal 686, Belém, Pará, Brasil.

WILLIAM E. BENSON has been appointed Program Director for Earth Sciences in the Division of Mathematical, Physical, and Engineering Sciences of the National Science Foundation in Washington. Dr. Benson joined the staff of the Foundation in January, 1956, and has served as Acting Program Director for Earth Sciences since September of last year. He will supervise the Foundation's program for research in earth sciences. During Fiscal Year 1957 the National Science Foundation made 54 grants, totaling $770,150, for basic research in the earth sciences.

EDWARD H. EAKLAND, JR. and ROBERT W. OSTERSTOCK announce their association as consulting mining geologists at 700 Newhouse Bldg., 10 Exchange Place, Salt Lake City, Utah. Mr. Eakland, Jr. was formerly with the American Metal Co. and the U. S. Geological Survey.

IAN CAMPBELL, Executive Officer of the Division of Geological Sciences, California Institute of Technology, succeeded J. Murray Luck, Professor of Biochemistry at Stanford, as President of the Pacific Division, A.A.A.S.; while Henry Eyring, Dean of the Graduate School of the University of Utah, became the new President-elect.

ANDRE L. BRICHANT has changed his address as follows: Adviser to the Director of Mines and Geology, Ministry of National Economy, Rabat, Morocco. Formerly he was Adviser to the State Planning Bureau in Jakarta, Indonesia.

ADVERTISEMENTS

Patrons of this journal are requested to refer to ECONOMIC GEOLOGY AND THE BULLETIN OF THE SOCIETY OF ECONOMIC GEOLOGISTS when consulting advertisers.

PLEASE TAKE NOTICE

For "BOOKS IN GEOLOGICAL SCIENCES"—a list of current and standard books on geology and related fields—available for purchase thru Economic Geology Business Office, 105 Natural Resources Bldg., Urbana, Illinois, see back pages of the No. 1, or February, 1957 issue and No. 5, or August, 1957 issue.

TABLES FOR MICROSCOPIC AND X-RAY IDENTIFICATION OF ORE MINERALS

By Alexander Novitzky

In Spanish. Pp. 270, 32 x 24 cm., linotype composition, paper bound. Price $12.

For orders: Economic Geology.

WILEY BOOKS

Two important new titles in geology . . .

PRINCIPLES OF STRATIGRAPHY

By CARL O. DUNBAR *and* JOHN RODGERS, *both of Yale University.* This book marks the first attempt since Grabau's, in 1913, to unify the enormous and diverse literature on stratigraphy. It approaches the subject from the point of view of the principles used in (1) describing the strata as they occur in sequence in local areas, (2) correlating these local sections, and (3) interpreting the stratigraphic records—both rocks and contained fossils—in terms of the past history of the earth.

The coverage begins with a discussion of the environments of deposition, followed by a presentation of the basic stratigraphic relations—including stratification, breaks in the record, and facies and facies change. The authors then consider the interpretation of specific lithotopes. The final section of the book treats synthesis, covering such topics as the local section, correlation, the stratigraphic system, and broad patterns in the distribution of sedimentary rocks.

All principles are illustrated inductively by examples from the stratigraphic record; the emphasis throughout is on synthesis and the interpretation of data. More than 130 carefully chosen illustrations and photographs accompany the text. They include many maps and cross sections showing sedimentary environments and stratigraphic relations. Critical parts of all drawings and of many photographs are clearly labeled to ensure easy comprehension. *1957. 356 pages. $10.00.*

A TREATISE ON LIMNOLOGY

Vol. I—Geography, Physics and Chemistry

By G. EVELYN HUTCHINSON, *Yale University.* Gives a thorough account of the sequence of geological, physical, chemical, and biological events that operate together in a lake basin. The book is an invaluable reference for geologists who want to know something of modern lakes in order to interpret the record of inland waters in past times. The second volume of the treatise will deal with limnobiology and the ecological, typological, and stratigraphic problems of lake development. *1957. Approx. 925 pages. Prob. $18.00.*

Send today for your examination copies.

JOHN WILEY & SONS, Inc.

440-4th Ave., New York 16, N. Y.

FIFTIETH ANNIVERSARY VOLUME

ECONOMIC GEOLOGY

1905–1955

CONTENTS

Part I

FOREWORD ii
ECONOMIC GEOLOGY ..... *Alan M. Bateman* 1
METALLOGENETIC PROVINCES AND EPOCHS ..... *F. S. Turneaure* 38
THERMAL SPRINGS AND EPITHERMAL ORE DEPOSITS ..... *Donald E. White* 99
THE CLASSIFICATION OF ORE DEPOSITS ..... *James A. Noble* 155
STRUCTURE OF HYDROTHERMAL ORE DEPOSITS ..... *H. E. McKinstry* 170
THE ZONAL THEORY OF ORE DEPOSITS ..... *Charles F. Park, Jr.* 226
TEMPERATURES IN AND NEAR INTRUSIONS ..... *T. S. Lovering* 249
SYNTHETIC MINERALS ..... *W. A. Weyl* 282
HYDROTHERMAL ALTERATION AS A GUIDE TO ORE ..... *George M. Schwartz* 300
OXIDATION OF COPPER SULFIDES AND SECONDARY SULFIDE ENRICHMENT ..... *Charles A. Anderson* 324
METHODS AND PROBLEMS OF GEOLOGIC THERMOMETRY ..... *Earl Ingerson* 341
SEDIMENTARY DEPOSITS OF RARE METALS ..... *Konrad B. Krauskopf* 411
ORIGIN OF URANIUM DEPOSITS ..... *V. E. McKelvey, D. L. Everhart and R. M. Garrels* 464

Part II

ENGINEERING GEOLOGY—A FIFTY YEAR REVIEW ..... *Robert F. Legget* 534
INFLUENCE OF GEOLOGICAL FACTORS ON THE ENGINEERING PROPERTIES OF SEDIMENTS ..... *Karl Terzaghi* 557
RECENT DEVELOPMENTS IN CLAY MINERALOGY AND TECHNOLOGY ..... *Ralph E. Grim* 619
PROPERTIES OF CALCIUM AND MAGNESIUM CARBONATES AND THEIR BEARING ON SOME USES OF CARBONATE ROCKS ..... *D. L. Graf and J. E. Lamar* 639
THE QUANTITATIVE APPROACH TO GROUND-WATER INVESTIGATIONS ..... *John G. Ferris and A. Nelson Sayre* 714
TIME OF PETROLEUM ACCUMULATION ..... *A. I. Levorsen* 748
COAL PETROLOGY ..... *C. E. Marshall* 757
THE USE OF GAMMA RAY MEASUREMENTS IN PROSPECTING ..... *William L. Russell* 835
ECONOMIC APPLICATIONS OF PALEOECOLOGY ..... *Samuel P. Ellison* 867
GEOPHYSICS APPLIED TO PROSPECTING FOR ORES ..... *Louis B. Slichter* 885
MINOR ELEMENTS IN SOME SULFIDE MINERALS ..... *Michael Fleischer* 970
THE STUDY OF PEGMATITE DEPOSITS ..... *Richard H. Jahns* 1025–1130

Order from:

ECONOMIC GEOLOGY PUBLISHING COMPANY

105 Natural Resources Building, Urbana, Illinois

Price to Subscribers (including members, non-member Journal subscribers, and students whether subscribers or not) $6.00

Price to Non-Subscribers to Journal 8.00

A COMPLETE PRINTING SERVICE

GOOD PRINTING does not just happen; it is the result of careful planning. The knowledge of our craftsmen, who for many years have been handling details of composition, proofreading, presswork and binding, is at your disposal. For seventy-five years we have been printers of scientific and technical journals, books, theses, dissertations and works in foreign languages. Consult us about your next printing job.

• PRINTERS OF • ECONOMIC GEOLOGY

LANCASTER PRESS, Inc.

PRINTERS • BINDERS • ELECTROTYPERS

ESTABLISHED 1877 LANCASTER, PA.

Announcing

SPECIAL STUDENT SUBSCRIPTION RATES

ECONOMIC GEOLOGY

and the Bulletin of the Society of Economic Geologists:

An international journal devoted to the field of Economic Geology

Edited by ALAN M. BATEMAN

Business Editor, MORRIS M. LEIGHTON

8 issues per year

Regular subscription rate, $6.50, student rate, $4.00

(Canadian postage, 30¢)

Students registered in geology courses in the United States and Canada may send for application blank to: **Economic Geology Publishing Company, 105 Natural Resources Building, Urbana, Illinois.**

for precision microscopy with polarized light

Leitz **POLARIZING** *microscopes*

In such fields as geology, mineralogy, petrography, coal research, plastics, biology, chemistry and biochemistry, there is a Leitz *POLARIZING* Microscope designed to meet every requirement. No other manufacturer offers such a wide variety of polarizing microscopes and accessories, built to the highest standards of quality and design.

Leitz polarizing microscope, Model AM

- Rotating anastigmatic tube analyzer for improved image quality and freedom from eyestrain.
- Polarizing tube accommodates large field-of-view eyepieces.
- Bertrand auxiliary lens with iris diaphragm can be raised and lowered.
- Rapid clutch changer and centering device for permanent centering of objectives.
- Large substage illuminating apparatus with two-diaphragm condenser and polarizer, either calcite or filter.
- Rotating object stage on ball bearings, with vernier reading to 1/10th°
- Rack and pinion motion for raising and lowering stage, to accommodate large opaque specimens.
- Polarizing vertical illuminator easily attachable.

E. LEITZ, INC., Dept. Q-11
468 Fourth Ave., New York 16, N. Y.

Please send brochure on Leitz *POLARIZING* Microscopes.

Name_____

Street_____

City_____ Zone____ State_____

05555

E. LEITZ, INC., 468 FOURTH AVENUE, NEW YORK 16, N. Y.
Distributors of the world-famous products of Ernst Leitz, Wetzlar, Germany
LENSES • CAMERAS • MICROSCOPES • BINOCULARS

AVAILABLE—ORDER NOW!

ECONOMIC GEOLOGY JOURNAL
INDEX TO VOLS. XLI-L
(1946 - 1955)

Price $3.00

ORDER FORM

To: Economic Geology Publishing Company
105 Natural Resources Building
Urbana, Illinois

Please enter my order for _____ copies @ $3.00 each

Payment _____ enclosed

Please bill me _____

Send copy to: _____

_____

_____

ANNOTATED BIBLIOGRAPHIES OF ECONOMIC GEOLOGY

Available—Vols. I-XXVIII (1928-1955).

Vol. XXIX (1956) current volume for 1957.

Price $5.00 per volume anywhere in the world thru Volume 27.
Effective Volume 28—price change to $6 per volume.

General Index, Vols. I-XXV, in preparation.

Order now from

ECONOMIC GEOLOGY PUBLISHING COMPANY

105 Natural Resources Building Urbana, Illinois

ECONOMIC GEOLOGY JOURNAL INDEX to Vols. XXXI-XL (1936-1945)—published September, 1947
Price $2.00

Also available Index to Vols. I-XX (1906-1926) —$3.00
Index to Vols. XXI-XXX (1927-1935)— 2.00
Index to Vols. XXXI-XL (1936-1945)— 2.00
Index to Vols. XLI-L (1946-1955) — 3.00

ECONOMIC GEOLOGY PUBLISHING COMPANY

105 Natural Resources Building Urbana, Illinois

FOR SALE

BACK VOLUMES OF ECONOMIC GEOLOGY

From Stock:

Complete Volumes: 3, 6, 7, 8, 9, 10, 11, 15, 22, 25 @ $15 per volume

Complete Volumes: 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50 @ $12 per volume

Incomplete Volumes but from which certain issues are still available (some of them almost complete):
1, 2, 4, 5, 12, 13, 14, 16, 17, 18, 19, 21, 23, 24 @ $2.25 per issue

Also shelf worn copies of scattered numbers thruout the series @ 75¢ per copy

Inquire:

Economic Geology Publishing Company
105 Natural Resources Building
Urbana, Illinois

Economic Geology issues devoted to articles on uranium or containing an article thereon:

VOL. 51, No. 1—ROGER Y. ANDERSON and EDWIN B. KURTZ, JR.: **A Method for the Determination of Alpha-Radioactivity in Plants as a Tool for Uranium Prospecting** $2.25

VOL. 51, No. 2—PAUL B. BARTON, JR.: **Fixation of Uranium in the Oxidized Base Metal Ores of the Goodsprings District, Clark Co., Nevada** 2.25

VOL. 51, No. 3—GEORGE W. WALKER and FRANK W. OSTERWALD: **Uraniferous Magnetite-Hematite Deposit at the Prince Mine, Lincoln County, New Mexico** 2.25

VOL. 51, No. 4—J. RADE: **Notes on the Geotectonics and Uranium Mineralization in the Northern Part of the Northern Territory, Australia** 2.25

VOL. 51, No. 4—GEORGE E. BOCRAFT: **Uranium Deposits of the Northern Part of the Boulder Batholith, Montana** 2.25

VOL. 51, No. 6—JOHN W. GRUNER: **Concentration of Uranium in Sediments by Multiple Migration-Accretion** 2.25

VOL. 51, No. 6—R. S. MATHESON and R. A. SEARL: **Mary Kathleen Uranium Deposit, Mount Isa-Cloncurry District, Queensland, Australia** 2.25

VOL. 51, No. 7—EUGENE B. GROSS: **Mineralogy and Paragenesis of the Uranium Ore, Mi Vida Mine, San Juan County, Utah** 2.25

VOL. 50, No. 2—**Uranium Issues** (12 articles on uranium) 2.25

VOL. 46, No. 4—WILLIAM L. RUSSELL and S. A. SCHERBATSKOY: **The Use of Sensitive Gamma Ray Detectors in Prospecting** 2.25

Order from:

Economic Geology Publishing Company
105 Natural Resources Bldg.
Urbana, Illinois

INTERNATIONAL UNION OF GEODESY AND GEOPHYSICS

BULLETIN GEODESIQUE

Quarterly Journal published by the Central Office of the International Association of Geodesy, 19, rue Auber, Paris, FRANCE

The scientific articles appearing in the BULLETIN GEODESIQUE are prepared by the foremost geodesists and geophysicists in the world and deal with the following subjects: *Mathematical geodesy* (*instruments, observations, calculation and adjustment of triangulation*), *Astronomical determination of geographic positions, Dynamical geodesy* (*gravimetry, figure of the Earth, earth tides, isostasy, etc.*) *Leveling.* It contains also a section of book notices.

Application for subscription to be addressed to: International Association of Geodesy, 19, rue Auber, PARIS, 9e. Annual subscription: $2.65 (payable by check drawn to the order of the International Association of Geodesy, the remittance to be sent to the International Association of Geodesy, care American Geophysical Union, 1530 P Street N W. WASHINGTON 5, D C.) or 13 shillings (payable by a deposit in sterling to the credit of the "Association Internationale de Géodésie" at the National Provincial Bank, Avenue Branch, SOUTHAMPTON, England.)

COMPREHENSIVE INDEX

OF THE PUBLICATIONS OF THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS, 1917–1945

By **DAISY WINIFRED HEATH**

603 PAGES. PRICE $4.00 (TO MEMBERS, $3.00)

THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
Box 979, Tulsa 1, Oklahoma

LABORATORY FOR ROCK ANALYSIS

Chemical analyses of rocks and minerals made with accuracy required for research. Commercial work cannot be accepted.

SAMUEL S. GOLDICH, in charge
Department of Geology and Mineralogy, University of Minnesota, Minneapolis 14, Minnesota

---

ROCK THIN SECTIONS
•
MOUNTED ORE SECTIONS

Fred Roberts » » »
PETROGRAPHIC SECTION SERVICE
2636½ W. MAIN ST., ALHAMBRA, CALIFORNIA

SWAN ENGRAVING COMPANY
PHOTO ENGRAVERS COMMERCIAL ARTISTS
BRIDGEPORT, CONN. NEW HAVEN, CONN
POUGHKEEPSIE, N.Y.

Geophysics for Economic Geologists

GEOPHYSICAL CASE HISTORIES, VOLUME I (1948)	$7.00
GEOPHYSICAL CASE HISTORIES, VOLUME II (1956)	$7.00
CUMULATIVE INDEX, 1931–1953 (All publications)	$4.00
GEOPHYSICS (Quarterly)	Per year $10.00

Detailed list of publications on request

Send Order with Remittance to

SOCIETY OF EXPLORATION GEOPHYSICISTS
Box 1536 Tulsa 1, Oklahoma

An A.A.P.G. Book!

POSSIBLE FUTURE PETROLEUM PROVINCES OF NORTH AMERICA

UP-TO-DATE PICTURE OF UNDISCOVERED RESOURCES, SYMPOSIUM REPRESENTING THE WORK OF 17 GEOLOGICAL SOCIETIES, 13 FEDERAL, STATE, AND PROVINCIAL GEOLOGICAL SURVEYS, OR ANALOGOUS ORGANIZATIONS, REPRESENTATIVES OF 33 OR MORE OIL COMPANIES AND 8 UNIVERSITIES, AND 24 CONSULTING GEOLOGISTS.

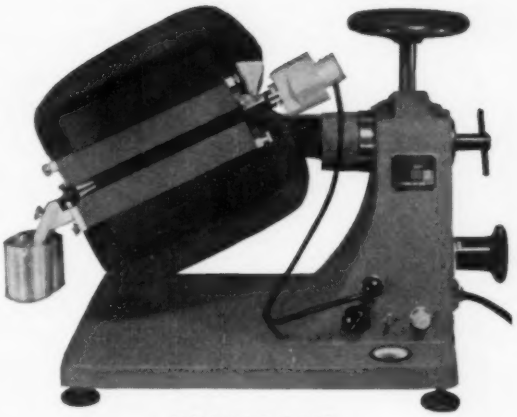
- First published in A.A.P.G. Bulletin, February, 1951
- Complete symposium, 6 x 9 inches, bound in cloth
- 360 pages, 153 line drawings

PRICE: $4.00 POSTPAID
(Member price, $2.50)

THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
BOX 979, TULSA 1, OKLAHOMA, U.S.A.

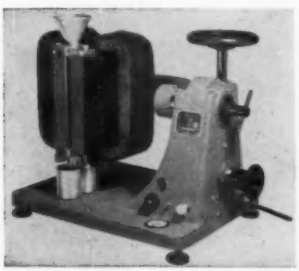
FRANTZ ISODYNAMIC Magnetic SEPARATOR

The variety of separations made possible by the ISODYNAMIC Magnetic Separator is practically infinite. Its use is limited only by the great number of magnetic minerals in nature—even many not usually thought of as magnetic—and their range of susceptibilities.



INCLINED FEED

Peculiar to the ISODYNAMIC Separator is the special configuration of the pole pieces which accounts for its exceptional selectivity. This results in a constant force on a particle of given susceptibility, regardless of its position in the operating space.



Vertical Feed

For more complete information, write for Bulletin 132-I.

S. G. FRANTZ Co., Inc. . . . Engineers

P.O. Box 1138
Trenton 6, New Jersey, U.S.A.

Cable Address:
MAGSEP, Trentonnewjersey

A GLOSSARY OF GEOLOGY
AND
RELATED SCIENCES

published by the

AMERICAN GEOLOGICAL INSTITUTE

A cooperative project of the AGI and its member societies, with more than 90 specialists contributing to its compilation. J. V. HOWELL, CHAIRMAN, AGI Glossary Project.

Contains nearly 14,000 terms used in theoretical and applied geology and geophysics.

- cloth bound
- about 350 pages
- 7 × 10 inches
- 25 fields covered . . .

COAL GEOLOGY
ENGINEERING GEOLOGY
GEOCHEMISTRY
GEOMORPHOLOGY
GEOPHYSICS
GLACIAL GEOLOGY
GLACIOLOGY
HYDROLOGY
INVERTEBRATE PALEONTOLOGY (except morphologic terms)
MARINE GEOLOGY
METEOROLOGY
MILITARY GEOLOGY
MINERALOGY
NUCLEAR GEOLOGY
ORE DEPOSITS
PALEOBOTANY
PERMAFROST
PETROLEUM GEOLOGY
PETROLOGY
SEDIMENTOLOGY
SEISMOLOGY
SPELEOLOGY
STRATIGRAPHY (except stratigraphic names)
STRUCTURE
SURVEYING & MAPPING

PRICE $6.00 U. S. *postpaid*
PAYMENT MUST ACCOMPANY ORDER

Order from
AMERICAN GEOLOGICAL INSTITUTE
2101 Constitution Avenue, N.W.,
Washington 25, D. C.